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Effects of inorganic cations on the rheology of aqueous welan, xanthan, gellan solutions and their mixtures

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ABSTRACT

The effects of different inorganic cations (Na^+, K^+, Ca^{2+} and Al^{3+}) on the rheological properties of single and mixture polysaccharide solutions have been systematically investigated. The apparent viscosity and viscoelasticity of welan solutions decrease with the addition of inorganic cations. Meanwhile, the addition of Al^{3+} and K^+, respectively, enhances the apparent viscosity and viscoelasticity of xanthan and gellan solutions by promoting the gelation. The viscosity retention rate of welan/xanthan mixtures is higher than that of the single components in Na^+, K^+ and Ca^{2+} solutions, and the viscosity retention rate of welan/gellan mixtures is higher than that of the single components in Ca^{2+} solutions. The salt induced gelation expands the application for polysaccharides, and it is also believed that the method of combining welan and xanthan (or gellan) is an effective strategy to control the rheology and morphology of solutions in the presence of inorganic salts.

1. Introduction

Microbial polysaccharides are widely employed in terms of thickening, emulsifying, stabilizing and gelation, due to their special physical and chemical properties (Hamcerencu, Desbrieres, Popa & Riess, 2009; Maruyama, Mikami, Hashimoto & Murata, 2007; Moreira, Coimbra, Nunes, Simoes, & Domingues, 2011; Paul, Morin & Monsan, 1986). Furthermore, microbial polysaccharides are both biocompatible and biodegradable, and are expected to be renewable resources, which can act as alternatives to products in the chemical industry.

To date, several bacteria have been found to be capable of secreting polysaccharides. Welan is a microbial polysaccharide, secreted by *Alcaligenes* sp., which consists of a pentasaccharide repeating unit, β-1,3-D-glucopyranosyl, β-1,4-D-glucuronopyranosyl, β-1,4-D-glucopyranosyl and α-1,4-L-rhamnopyranosyl, and a single monosaccharide side-chain at the O-3 of the 4-linked glucopyranosyl. The monosaccharide may be either L-rhamnopyranosyl or L-mannopyranosyl, in the approximate ratio of 2:1, and about half, or more, of the repeating units have acetyl and glyceryl substituents (Rinaudo, 2004; Tako, Teruya, Tamaki & Konishi, 2009).

Xanthan is a high molecular extracellular polysaccharide, produced by the bacterium Xanthomonas campestris, which has a cellulosic backbone consisting of five monosaccharides, to give a pentasaccharide repeating unit. The cellulosic backbone is substituted at C-3 on alternate β-1,4-D-glucopyranosyl residues with trisaccharide side chains of β-D-rhamnopyranosyl, β-1,4-D-glucuronopyranosyl and α-1,2-D-mannopyranosyl, with various amounts of acetyl and pyruvate substituents (De Jong & Van de Velde, 2007; Mukherjee, Sarkar & Moulik, 2010; Rodd, Dunstan & Boger, 2000). Gellan is a linear, anionic heteropolysaccharide produced by the microorganism *Sphingomonas elodea*. The structure is based on a tetrasaccharide repeating unit composed of (1-3)-b-D-glucose, (1-4)-b-D-glucuronic acid, (1-4)-b-D-glucose, and (1-4)-a-L-rhamnose as the backbone (Jansson, Lindberg & Sandford, 1983; Whittaker, Al-Ruqaie, Kasapis & Richardson, 1997).

Recently, polysaccharides have increasingly attracted more attention for their applications in the petroleum industry (Sun et al., 2011; Xu et al., 2014). They can be used to improve the sweep efficiency in enhanced oil recovery (EOR), due to their ability to control water mobility and reduce the permeability in a reservoir by increasing the viscosity of the injected fluid. However, the presence of mineralized ions in the formation water usually reduces the viscosity of the polymers used (Saadatabadi, Nourani & Emadi, 2010), reducing the displacement efficiency. Therefore, it is very important to study the influence of inorganic ions on the properties of polysaccharides. The intrinsic viscosity of Balangu seed gum, studied by Mohammad Amini and Razavi (2012) was markedly

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reduced by the presence of NaCl, and decreased by increasing the ionic strength of the solution. Ma and Pawlik (2007) found that, at higher electrolyte concentrations (≥0.1 M), the state of the guar aggregation depended on the kosmotropic or chaotropic properties of the background electrolytes. The presence of strongly chaotropic ions, such as K^+ and Cs^+, seemed to induce the dissolution of guar aggregates into individual molecules. Contrary to this, guar chains underwent an even more extensive aggregation in the presence of Kosmotropic ions, such as Li^+ and Na^+, forming larger structures, which resulted in higher intrinsic viscosities. Synergistic interactions may occur by blending different biopolymers, which always results in the optimization of the physical and chemical properties of the mixtures, such as enhancing the viscosity, gelation, and so on (Fitzpatrick, Meadows, Ratcliffe & Williams, 2013). Lopes, Andrade, Milas and Rinaudo (1992) reported that a small synergistic effect occurred between xanthan and guar in 20 mM NaCl, and that the effect became more pronounced in water. They concluded that xanthan adopted a disordered conformation in water, whereas the conformation was in an ordered form in 20 mM NaCl. Similar results were reported by Dalbe (1992). They studied xanthan/glucomannan mixtures using a small deformation oscillation method, and reported that a dramatic decrease in gel strength was caused by the addition of 85.55 mM NaCl or 67.07 mM KCl to the mixtures, but not with the further addition of electrolytes. Also, Wang, Wang and Sun (2002) noticed that a decrease in the viscosity of xanthan/LBG mixture solutions was associated with the addition of 40 mM NaCl. Khouryieh, Herald, Aramouni and Alavi (2007) reported that the intermolecular interaction occurred between xanthan and guar in 2 mM NaCl, but did not occur in 40 mM NaCl, from which it was inferred that the degree of disordering of xanthan played a critical role in xanthan/guar mixtures.

From the above, we know that most polysaccharides show a reduction in viscosity upon encountering mineralized water. However, different mineral ions may have different effects on the viscosity of the polysaccharide solutions. Much work has focused on the effect of monovalent ions on the properties of polysaccharides, and their inherent viscoelastic properties; the evaluation of polysaccharides in solution has been studied to a lesser extent. Therefore, in this study, the effects of different valent inorganic cations (Na^+, K^+, Ca^{2+} and Al^{3+}) on the apparent viscosity and viscoelasticity of aqueous welan, xanthan, gellan solutions, and their mixtures, have been investigated in detail, using the steady-state shear and dynamic oscillation methods. The aim of this study is to provide basic data and a theory base for the application of biopolymers in EOR.

2. Experimental

2.1. Materials

Welan was supplied by the Food Fermentation Industry Research Institute of Shandong Province, China. The average molecular weight was approximately 6.6×10^5 g mol^{-1}. Xanthan (FUFENG 80) was produced by Inner Mongolia Fufeng Biotechnology Co., Ltd. The average molecular weight was approximately 2.0×10^6 g mol^{-1}. Gellan was purchased from the Zhengzhou Chemical Co., Ltd. The average molecular weight was approximately 7.0×10^5 g mol^{-1}. The intrinsic viscosities of welan, xanthan and gellan were 6479, 7627 and 1444 mL g^{-1}, respectively, determined by the Ubbelohde viscometer at 25 °C. NaCl, KCl, $CaCl_2$, and $AlCl_3$, purchased from the Sinopharm Chemical Reagent Co., Ltd., China, were all of the reagent grade. Water used in the experiment was triply distilled by a quartz water purification system. The structures of welan, xanthan and gellan are depicted in Fig. 1.

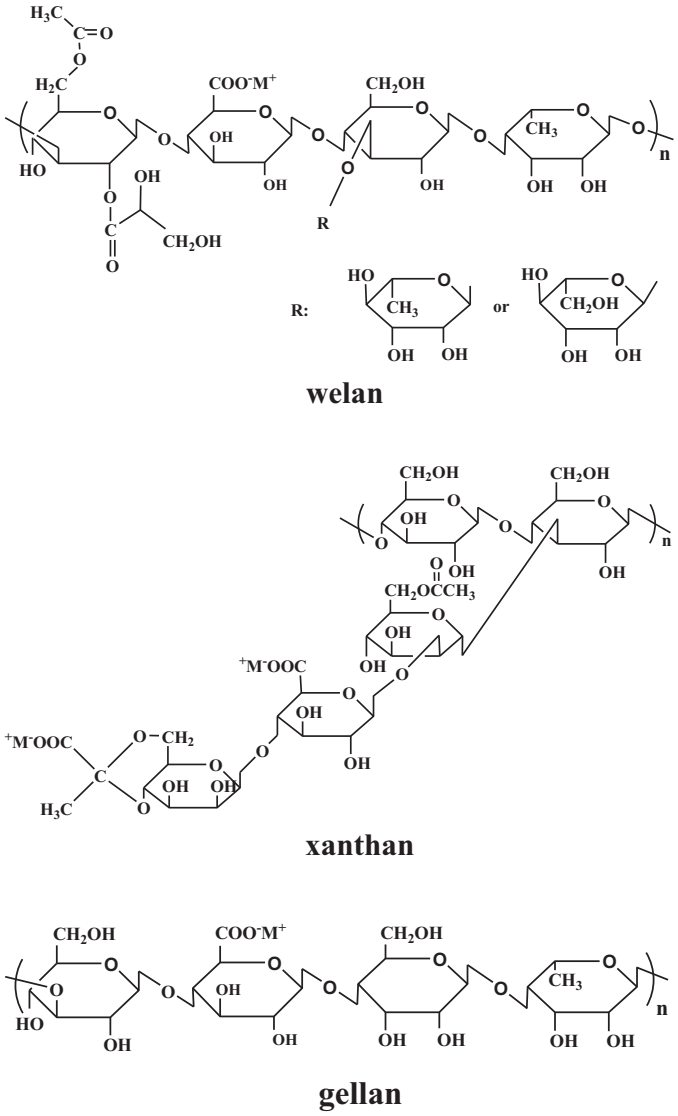

Fig. 1. Structures of welan, xanthan and gellan.

2.2. Preparation of polysaccharide solutions

The stock solutions were prepared by dispersing dry samples in distilled water, while continuously stirring, at the ambient temperature. The experimental solutions were obtained by diluting the stock solutions. The percentage content of welan in the mixtures was changed from 0% to 100%, and the concentrations of the mixtures were fixed at 1750 mg L^{-1}. To study the effects of different valent inorganic cations on polysaccharides, appropriate amounts of NaCl, KCl, $CaCl_2$ and $AlCl_3$ were added and completely dissolved to make salt solutions of 50 mM inorganic strength.

2.3. Rheological measurements

In rheology, the intrinsic viscosity is a useful experimental parameter in studying the inherent characteristic of the polymer aqueous solutions. The intrinsic viscosity reflects the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the molecular chains in the solvent (Lai & Chiang, 2002). When the polymer chains are separate, the intrinsic viscosity of a polymer in solution depends only on the dimensions of the molecular chain. Consequently, the intrinsic viscosity provides insight into

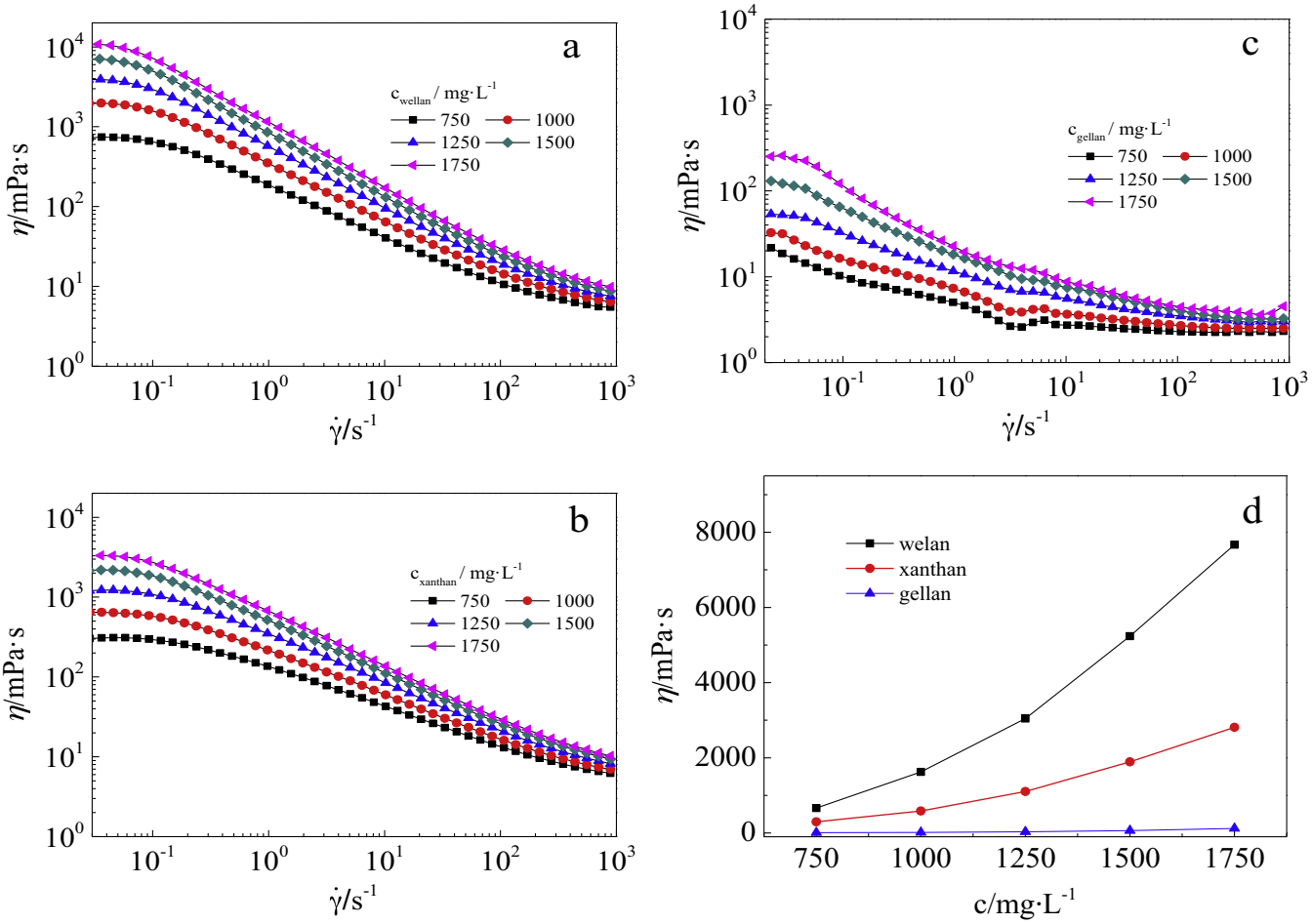

Fig. 2. The apparent viscosities (η) of aqueous (a) welan, (b) xanthan and (c) gellan solutions as a function of the shear rate at different concentrations. (d) Variation of η of aqueous welan, xanthan and gellan solutions, with increasing concentrations, at shear rate of 0.1 s^{-1}.

the molecular characteristics of a biopolymer (Khouryieh et al., 2007).

The intrinsic viscosity is determined through extrapolation to infinite dilution, according to the Huggins empirical expression (Huggins, 1942):

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \tag{1}$$

where k is the Huggins constant, C is the polymer concentration, and $[\eta]$ and η_{sp} are the intrinsic viscosity and the specific viscosity, respectively. Extrapolation to zero concentration is determined by plotting η_{sp}/C vs C, which would result in straight lines:

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} \tag{2}$$

The specific viscosity (η_{sp}) in Eqs. (1) and (2) is defined as:

$$\eta_{sp} = \frac{\eta}{\eta_s} - 1 \tag{3}$$

where η and η_s are the apparent viscosities of the solution and the solvent, respectively. In this study, the intrinsic viscosity $[\eta]$ was determined for each solution by measuring the apparent viscosities of polysaccharide solutions at different concentrations and shear rates.

The Maxwell model is widely used to describe the viscoelasticity of polymer solutions. It is a two-parameter model in which the storage modulus (G') and loss modulus (G'') can be described at all frequencies. The frequency dependence of G' and G'' is expressed in the following equations (Tam, Jenkins, Winnik & Bassett, 1998):

$$G' = G_0 \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \tag{4}$$

$$G'' = G_0 \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \tag{5}$$

where G_0 is the plateau modulus, τ_R is the relaxation time, $\omega = 2\pi f$ is the radian frequency, and f is the frequency in Hertz. G' and G'' reflect the viscous and elastic components of the solution samples, respectively.

The steady-state shear and dynamic oscillation measurements were carried out on a Haake MARS III Rheometer (Germany) with a coaxial cylinder sensor system, Z41-Ti. The maximum allowable temperature deviation was ±0.1 °C. Samples were kept stationary for more than 24 h before measuring, in order to guarantee that there were no bubbles in them. In the frequency oscillation, a stress of 0.1 Pa was selected to ensure that samples were within the linear viscoelastic region, and, the oscillatory frequency sweep was carried out within the frequency range of 0.01–10.00 Hz, in the oscillation mode OSC.

All of the measurements were performed at 25.0 ± 0.1 °C.

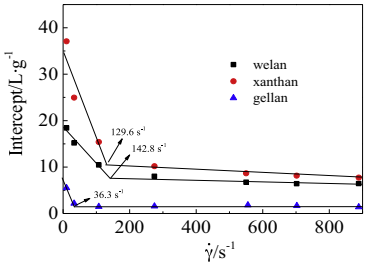

Fig. 3. Variation of the intercept with different shear rates. Lines are fitting curves.

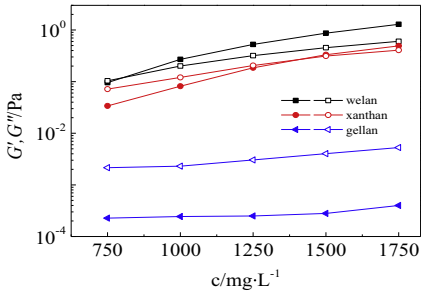

Fig. 4. Variation of the storage modulus (G', solid) and loss modulus (G'', hollow) of aqueous welan, xanthan and gellan solutions, with increasing concentrations, at the dynamic oscillating frequency of 0.1 Hz.

3. Results and discussion

3.1. The rheology of welan, xanthan and gellan in salt free water

The apparent viscosities of aqueous welan, xanthan and gellan solutions at different concentrations, investigated in the steady-sate shearing experiments, are plotted in Fig. 2a–c. The apparent viscosities of aqueous polysaccharide solutions gradually decrease with an increase in the shear rate. Namely, the polysaccharide system belongs to the typical pseudoplastic fluid. The shear thinning behavior of the polysaccharide system is related to the orientation of its macromolecules along the stream line of the flow (Chagas, Machado, Haag, De Souza, & Lucas, 2004). The stretching macromolecules of the polysaccharide intertwine to form aggregates in the low shear rate; the flow resistance of many aggregates results in the high viscosity. However, the aggregates will be destroyed as the shear rate increases, dispersing macromolecules along the flow direction, causing the apparent viscosity to decrease as a result. Fig. 2d shows the effects of concentration on the apparent viscosities of aqueous welan, xanthan and gellan solutions at the shear rate of 0.1 s^{-1}. The apparent viscosities of welan and xanthan solutions increase with increasing the concentration, while that of gellan solutions is only increased slightly. At the same concentration, the apparent viscosity of welan is the highest, that of gellan is the smallest, and that of xanthan is in between. Taking 1750 mg L^{-1} as an example concentration, the apparent viscosity of welan (7665 mPa s) is nearly 60 times of that of gellan (2776 mPa s), and 2.7 times of that of xanthan (128 mPa s). The thickening capability of welan is stronger than that of both xanthan and gellan, which can be attributed to the significant difference in their chain arrangement. This is can be inferred from the intrinsic viscosity of aqueous welan, xanthan and gellan solutions, as shown in Fig. 3. Using Eqs. (2) and (3), the intercepts in Eq. (1) at different polysaccharide concentrations and shear rates can be obtained. Because the intrinsic viscosity depends only on the dimensions of the separate molecular chains, it becomes constant when the aggregation transitions to separate molecules. Consequently, the inflection of the intercept represents the conformation transition of the polysaccharide molecules in solutions. The intercept is the intrinsic viscosity when the molecular chain is separate. The intrinsic viscosities of aqueous welan, xanthan and gellan solutions are 6.3 L g^{-1}, 7.8 L g^{-1} and 1.4 L g^{-1}, respectively, which are consistent with the results measured using the Ubbelohde viscometer. The shear rate, corresponding to the inflection, is defined as the critical shear rate. The critical shear rate values of welan, xanthan and gellan are 142.8 s^{-1}, 129.6 s^{-1} and 36.3 s^{-1}, respectively, indicating that the molecular aggregation of welan can bear higher stress. Welan has a stronger intramolecular interaction than the random-coil conformation of xanthan and gellan, which may increase the chain dimensions, resulting in a higher viscosity.

The macromolecular motion contains different microscopic motion hierarchies and forms. Frequency scanning is an important component of dynamic viscoelasticity experiments, which may characterize the features of the motion unit, including the variety of different molecules, coils and chain segments within the specimen system (Gopakumar, Lee, Kontopoulou & Parent, 2002; Xin, Xu, Gong, Bai, & Tan, 2008). Fig. S1, in the supporting information, shows the storage modulus (G') and loss modulus (G'') as a function of the frequency for aqueous welan, xanthan and gellan solutions. G' and G'' represent elasticity and viscosity of an aqueous polysaccharide solution, respectively. Fig. 4 shows G' and G'' of aqueous welan, xanthan and gellan solutions at the dynamic oscillating frequency of 0.1 Hz. The dynamic modulus of the aqueous polysaccharide solutions increases with the increasing polysaccharide concentration. G' of welan is higher than G'' in the range of experimental concentrations, except for 750 mg L^{-1}. The elastic component is dominant in the viscoelasticity, indicating that a gel structure is formed. Differently than the welan solution, G' of gellan solution is lower than G'' in all experimental concentrations, showing the typical nature of ordered structure. Another characteristic of this structure is the strong dependence of the modulus on the frequency, as shown in Fig. S2. This rheological behavior indicates that viscosity is the main factor in the flow of the gellan solution. For the xanthan solution, when the concentration is lower than 1500 mg L^{-1}, G' is lower than G''. When the concentration exceeds 1500 mg L^{-1}, G' is higher than G''. Therefore, increasing concentration results in the xanthan solution gradually transforming from the viscous fluid to the elastomer; the solution exhibits a gel-like nature at high concentrations. G' and G'' of welan are higher than those of xanthan and gellan, indicating that the viscoelasticity of welan is the highest among the three polysaccharides. The intermolecular association of welan may take place between the methyl group of the L-rhamnosyl residue and the counter hemiacetal oxygen atom of the L-rhamnosyl residue on different molecules via van der Waals forces, and between side and backbone chains of different molecules by hydrogen bonding (Member & Morris, 1995; Morris, Gothard, Hember, Manning, & Robinson, 1996). It is possible that two or more double helices arrange in parallel, such as in the zipper model reported by Xu, Xu, Liu, Chen, and Gong (2013). While the helices of gellan are associated by weak interactions (Tako et al., 2009), and the network structure formed by xanthan is just a transient one (Choppe, Puaud, Nicolai & Benyahia, 2010).

3.2. Effects of inorganic cations on the rheology of aqueous welan, xanthan and gellan solutions

Generally, the addition of inorganic ions screens the electrostatic repulsion between charges along the backbone of the polyelectrolyte chain. The screening of the electrostatic interactions, in turn, allows the chain to fold up and assume a smaller, more compact structure. The degree to which a polyelectrolyte molecule's conformation shrinks may be dependent on the stiffness of the macromolecular chain in solution (Cohen & Priel, 1989; Wyatt, Gunther & Liberatore, 2011). Since the molecular

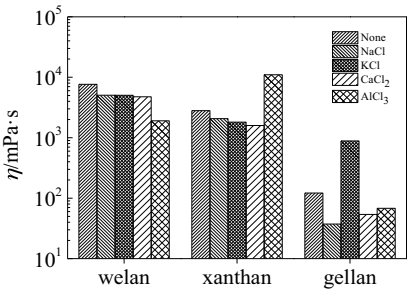

Fig. 5. Variation of the apparent viscosity (η) of aqueous welan, xanthan and gellan solutions, with the addition of different inorganic cations, at the shear rate of 0.1 s^{-1}. The polysaccharide concentration is 1750 mg L^{-1} and the ionic strength of salt solutions is 50 mM.

configuration changes, the solution rheology may also change. In most instances, the existence of inorganic salts is a disadvantage for the viscosity of the polyelectrolyte solutions, due to the electrostatic shielding of the inorganic ions. However, unlike the effects they have on the traditional polyelectrolytes, inorganic cations may have a distinct influence on the rheology of some polysaccharides.

The apparent viscosities of the aqueous welan, xanthan and gellan solutions as a function of the shear rate, with NaCl, KCl, $CaCl_2$ and $AlCl_3$, respectively, have been shown in Fig. S2. The ionic strength of salt solutions is 50 mM. The aqueous polysaccharide solutions still maintain the characteristics of the pseudoplastic fluid when different inorganic salts are added. Fig. 5 shows the apparent viscosities of welan, xanthan and gellan in water and inorganic salts at the shear rate of 0.1 s^{-1}. The apparent viscosity of welan solutions decreases in the presence of the salt, showing the typical behavior of polyelectrolytes. At an ionic strength of 50 mM, the order of the apparent viscosity values of welan in salt solutions is None > $Na^+ \approx K^+ > Ca^{2+} > Al^{3+}$. The viscosity retention rate (ϕ, the ratio of the viscosity in different inorganic cations and the viscosity in pure water) decreases with increasing the ionic strength, as shown in Table 1. The results indicate that the ionic strength is not an only determining factor in the apparent viscosity of the welan solution which also depends on the species of inorganic cation. While at the same ionic strength, the value of ϕ has a relationship with the valence of inorganic cations. The inorganic cation with high valence is easier to cause the reduction in the viscosity of welan solutions. The electrostatic repulsion between the charged groups of welan is screened by inorganic cations, allowing macromolecules to adopt a more compact conformation, and causing a reduction in the hydrodynamic size of the macromolecules (Jin et al., 2014; Samanta, Bera, Ojha & Mandal, 2010). The screening effect by the high valence inorganic cation like except Al^{3+} on the welan molecular structure is more intensive.

For xanthan, the variation of the apparent viscosity in salt solution is different from that of welan. The apparent viscosity of xanthan significantly increases in the $AlCl_3$ solution, even exceeding that of welan. At the same ionic strength, the order of the apparent viscosity value for xanthan in salt solutions is Al^{3+} > None > $Na^+ > K^+ > Ca^{2+}$. The value of ϕ of xanthan with Al^{3+} is 391.1%, which is far greater than that in other inorganic salts. In aqueous solutions, the structure of xanthan undergoes an order-disorder transition from helix to coil (Baradossi & Brant, 1982). This conformational transition is significantly affected by different inorganic cations. Xanthan is in the disordered conformation in salt free water, whereas, in Na^+, K^+ and Ca^{2+} solutions, xanthan starts to take on an ordered conformation, due to the charge screening effect. The screening effect of the divalent cation (Ca^{2+}) is more notable than those of the monovalent cations (Na^+ and K^+). Similar results were found by Zhong, Oostrom, Truex, Vermeul, and Szecsody (2013). For the conformation transition of xanthan in salt water, Rochefort and Middleman (1987) reported that a complete ordered conformation can be obtained in 10 mM NaCl for a 250 mg L^{-1} xanthan solution. In a study by Mohammed, Haque, Richardson and Morris (2007), the gel-like state of xanthan was disrupted when the concentration of Ca^{2+} ions was increased to 200% stoichiometric equivalence. However, in this study, the ordered conformation of xanthan did not occur in 50 mM Al^{3+}. Instead, molecules of xanthan tended to form a more dense conformation, which could be inferred by the gel-like appearance of the solution. Such an effect is mainly attributed to the fact that Al^{3+} acts as a cross-linker, which binds to individual carboxyl groups in the side chains of xanthan, thus favoring the conformation of the network. This phenomenon of xanthan in the Al^{3+} solution has not been reported in previous studies.

For gellan, the variation of the apparent viscosity in the salt solutions is more interesting. The maximum apparent viscosity of gellan appears in the K^+ solution, and, at the same ionic strength, the order of the apparent viscosity values in salt solutions is K^+ > None > $Al^{3+} > Ca^{2+} > Na^+$. The value of ϕ of gellan with K^+ is 726.5%, which is more than 7 times of that in salt free water, while values of ϕ in other inorganic cations are all less than 1. K^+ has a greater effect on both the structural and the rheological properties of gellan than the salt free water and other inorganic cations, even the multivalent cations. The presence of K^+ leads to the enhanced aggregation of gellan, due to competitive hydration between the polysaccharide chains and the cations. The conformational transition of gellan is accompanied by some network formation, producing a weak gel. This may be explained by the compatibility of potassium with the gellan helices, based on the structural similarity between the hydrodynamic radius of the cation and the cavity that the helices create, and also by the ordered arrangement of the cation along the helices (Funami et al., 2009; Matsukawa & Watanabe, 2007). The apparent viscosity of gellan is in direct proportion to the valence of the inorganic cation, except K^+. The higher the valence, the higher the viscosity retention rate. This indicates that complexation may occur between the molecules and the multivalent cations. Because there is no side chain in the molecular structure, the complexation is limited in crosslinking. This interaction only partially counteracts the viscosity loss caused by the electrostatic shielding.

The effects of the inorganic salts on the viscoelasticity of each polysaccharide solution are shown in Fig. S3. The viscoelasticity of welan solutions reduces in all inorganic salts, while the addition of $AlCl_3$ and KCl strengthens the viscoelasticity of xanthan and gellan solutions, respectively. These results further confirm the above conclusions. The salt induced gelation is attributed to the enhancement of the electrostatic attraction between negatively charged helices and positive ions. Addition of the inorganic salts can facilitate the association of charged helical structures in two different ways: by non-specific screening of the electrostatic repulsion between helices, and by the incorporation of counterions as an integral part of the aggregate structure, contributing to its stability through electrostatic attraction. Our present results indicate that the former is the dominant mechanism in the salt induced gelation of gellan, and that the latter corresponds to that of xanthan.

3.3. *Effects of inorganic cations on the rheology of the polysaccharide mixture solutions*

From the above, we know that the inorganic cations can promote the gelation of corresponding polysaccharides. However, the apparent viscosity and viscoelasticity of the polysaccharides decrease in some inorganic cation solutions, such as: welan in Na^+, K^+, Ca^{2+} and Al^{3+} solutions; xanthan in Na^+, K^+ and Ca^{2+} solutions; and, gellan in Na^+, Ca^{2+} and Al^{3+} solutions. Consequently, in order to mitigate these negative effects, the influence of inorganic cations on the rheological properties of the polysaccharide mixtures has

Table 1
The viscosity retention rate (ϕ/%) of the polysaccharides in different inorganic salts, at the shear rate of 0.1 s^{-1}. The concentrations of the single polysaccharides and polysaccharide mixtures are all of the 1750 mg L^{-1}.

Inorganic salts	Concentration/mM	Ionic strength/mM	Welan	Xanthan	Gellan	Welan/xanthan	Welan/gellan
None	0	0	100.0	100.0	100.0	100.0	100.0
NaCl	50	50	65.86	73.58	30.59	78.21	59.17
KCl	50	50	66.01	64.59	726.5	78.66	76.46
$CaCl_2$	16.67	50	62.99	56.67	44.13	74.16	65.07
$AlCl_3$	8.33	50	31.82	391.1	55.72	34.34	38.11
$CaCl_2$	50	150	53.11	49.78	40.86	66.99	55.93
$AlCl_3$	50	300	29.88	340.6	51.55	30.29	37.13

been investigated, especially welan mixtures, as studies on the mixtures between welan and other polysaccharides have been rarely reported so far. In this study, we mainly focus on the mixtures between welan and xanthan or gellan to explore the internal structural changes in polysaccharide mixtures with or without inorganic cations.

The apparent viscosities of welan/xanthan mixture and welan/gellan mixture have been investigated, as shown in Fig. S4. The rheological behavior of polysaccharide mixtures is similar to that of the single components. The apparent viscosities of the polysaccharide mixtures were plotted as a function of the welan fraction at the shear rate of 0.1 s^{-1} in Fig. 6. The apparent viscosities of the welan/xanthan mixture and welan/gellan mixture vary with the mass fraction of welan, increasing as the proportion of welan increases in the mixtures. The curves of the apparent viscosity vs welan fraction have two distinct parts: slow increase and rapid increase. The change in the slopes of the curves suggests that there is a change in the molecular structure of the mixtures. The increase in the apparent viscosities of the mixtures, in the later stage, can be attributed to the conformational transition of welan from a helical form to a more flexible form, because of binding. Consequently, welan plays a crucial role in controlling the apparent viscosities of the mixtures. The welan fractions, corresponding to the conformational change, are 73.8% and 66.7% for the welan/xanthan mixture and welan/gellan mixture, respectively.

The variation of the dynamic modulus (G' and G'') of the mixtures with the change of the dynamic oscillating frequency at different mass concentration ratios is shown in Fig. S5. Fig. 7 reveals the relationship between the dynamic modulus and the welan fraction. The addition of welan enhances the viscoelasticity of the mixtures, as the dynamic modulus increases with increasing the proportion of welan in the mixtures. When the welan fraction in the mixtures is small, G' is close to G'', especially in the welan/gellan mixtures. With the increase of the welan fraction, the growth of G' is faster than that of G'', indicating that the mixtures are more elastic than viscous, and that a net structure is gradually formed. The transition of the welan conformation outweighs the binding of xanthan or gellan

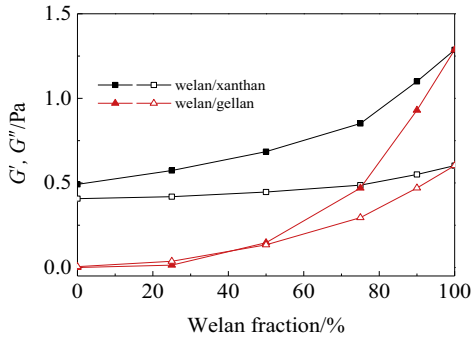

Fig. 7. The storage modulus (G', solid) and loss modulus (G'', hollow) as a function of welan fraction in welan/xanthan mixtures and welan/gellan mixtures at the dynamic oscillating frequency of 0.1 Hz.

to welan. These results suggest that the conformational change of welan is predominant in controlling the apparent viscosities and viscoelasticities of the mixtures.

Welan/xanthan mixture and welan/gellan mixture, with a mass concentration ratio of 50%:50%, were chosen to characterize the rheological behavior of polysaccharide mixtures in inorganic cations. As shown in Fig. 8, differences in the apparent viscosity were found between water and salt solutions for both the welan/xanthan mixture and welan/gellan mixture. In the salt solutions of 50 mM ionic strength, the apparent viscosities of welan/xanthan mixture and welan/gellan mixture decrease. However, the ϕ value of welan/xanthan mixtures is higher than that of welan or xanthan in NaCl, KCl and $CaCl_2$ solutions, as shown in Table 1. The ϕ value of welan/gellan mixtures is higher than that of welan or gellan in $CaCl_2$ solutions. The results indicate that a synergistic interaction may occur with Na^+, K^+ and Ca^{2+} in welan/xanthan mixtures, and with Ca^{2+} in welan/gellan mixtures. For the welan/xanthan mixture, the apparent viscosity in the $AlCl_3$ solution is the lowest, and the salt induced gelation of xanthan disappears. At the ionic strength of 50 mM, the ϕ value of the welan/xanthan mixture in the $AlCl_3$ solution is 34.34%, which is closer to the value of welan (31.82%), comparing with that of

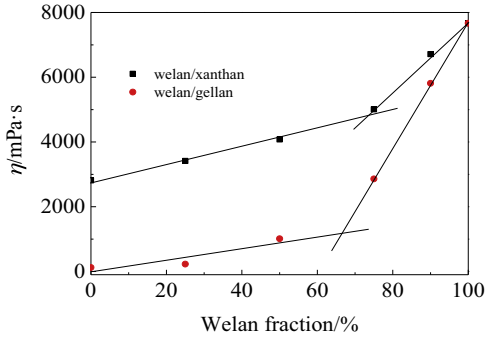

Fig. 6. The apparent viscosity (η) as a function of welan fraction in welan/xanthan mixtures and welan/gellan mixtures at the shear rate of 0.1 s^{-1}. Lines are fitting curves.

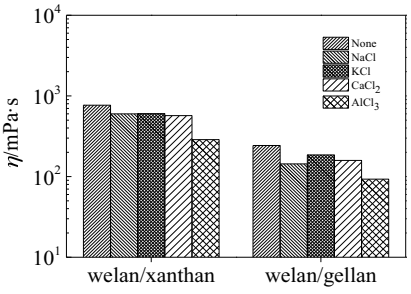

Fig. 8. Variation of the apparent viscosity (η) of welan/xanthan mixtures (50%:50%) and welan/gellan mixtures (50%:50%), with the addition of different inorganic cations, at the shear rate of 0.1 s^{-1}. The ionic strength of salt solutions is 50 mM.

xanthan (391.1%). The viscoelasticity variation of welan/xanthan mixtures, as shown in Fig. S6, further confirms the inference. A gradual transition of disorder to order in welan/xanthan mixtures occurs with increasing the ionic strength, and the screening of electrostatic repulsion between helices favors the ordered conformation. This behavior of the welan/xanthan mixture is similar to that of just welan in the salt solutions. Consequently, the conformational change of welan, in salt solutions, is the dominant factor affecting the rheology of the welan/xanthan mixtures. However, the salt induced gelation of gellan with K^+ still plays a positive effect in welan/gellan mixtures. The value of ϕ of the welan/gellan mixture (76.46%) is obviously higher than that of welan in the KCl solution (66.01%). At the same ionic strength, the ϕ value of the welan/gellan mixture with K^+ is higher than that with Na^+ (59.17%). This difference is mainly attributed to the salt induced gelation of gellan with K^+, which can be seen in Fig. S6. The viscoelasticity of the welan/xanthan mixtures decreases in the salt water, while it is higher in the KCl solution than that in other salt solutions.

4. Conclusions

The inorganic cations Al^{3+} and K^+ can promote the gelation of xanthan and gellan solutions, respectively, which greatly enhance the apparent viscosities and viscoelasticities. The addition of inorganic salts facilitate the association of charged helical structures in different ways: the salt induced gelation of xanthan is attributed to the complexation, and the salt induced gelation of gellan is caused by the competitive hydration. The finding of these systems expands the application of polysaccharides, in circumstances where inorganic salts exist.

In some inorganic cations, the apparent viscosities of welan, xanthan, and gellan decrease. However, the viscosity retention rate of welan/xanthan mixtures is higher than that of welan or xanthan in Na^+, K^+ and Ca^{2+} solutions. The viscosity retention rate of welan/gellan mixtures is higher than that of welan or gellan in Ca^{2+} solutions. Moreover, the salt induced gelation of gellan with K^+ still has a positive effect on welan/gellan mixtures. Synergistic interactions may occur in welan/xanthan mixtures and welan/gellan mixtures, in the specific inorganic cations. Consequently, the method of combining welan and xanthan (or gellan) is an effective strategy to control the rheology of solutions to be used in enhanced oil recovery field.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.12.030.

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