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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.

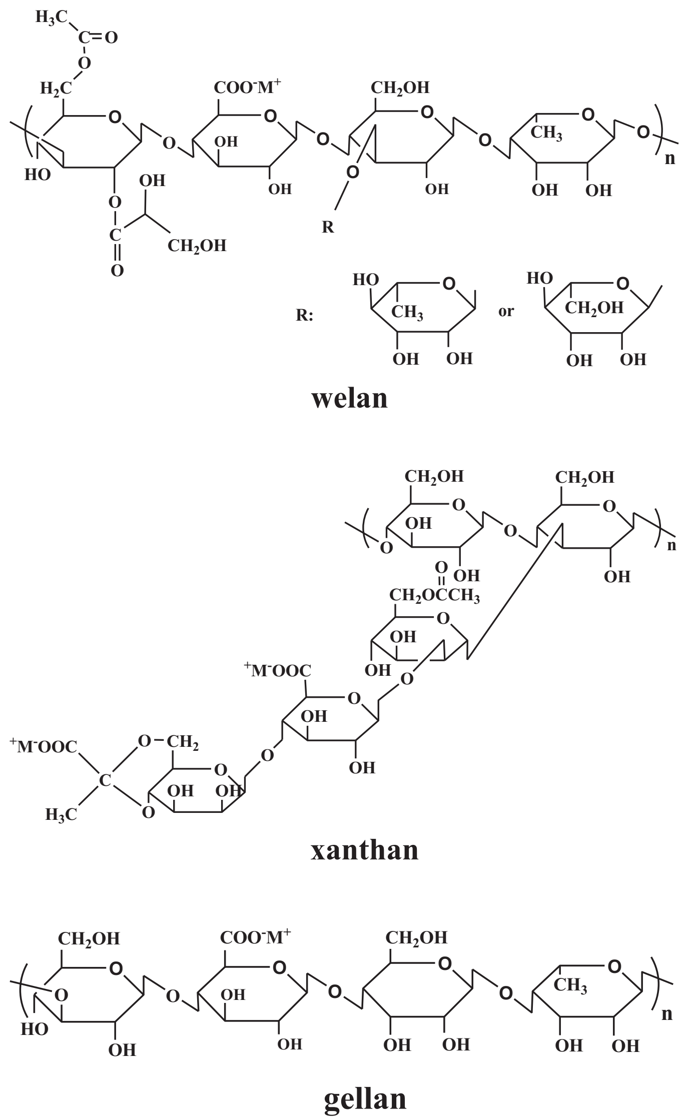

Fig. 1. Structures of welan, xanthan and gellan.

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