



Intrinsic viscosity and rheological properties of natural and substituted guar gums in seawater



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ABSTRACT

The intrinsic viscosity and rheological properties of guar gum (GG), hydroxypropyl guar (HPG) and carboxymethyl guar (CMG) in seawater and the effects of shear rate, concentration, temperature and pH on these properties were investigated. An intrinsic viscosity-increasing effect was observed with GG and HPG in seawater (SW) compared to deionized water (DW), whereas the intrinsic viscosity of CMG in seawater was much lower than that in DW due to a screening effect that reduced the repulsion between the polymer chains. Regardless of the functional groups, all sample solutions were well characterized by a modified Cross model that exhibited the transition from Newtonian to pseudoplastic in the low shear rate range at the concentrations of interest to industries, and their viscosity increased with the increase in their concentration but decreased with the increase in temperature. In contrast to nonionic GG or HPG, anionic CMG had a slightly decreased viscosity property in SW, exhibiting polyelectrolyte viscosity behavior. The α value in the zero-shear rate viscosity vs. concentration power-law equation for the samples gave the order of CMG > HPG > GG while the SW solution of CMG had the lowest viscous flow activation energy and exhibited a strong pH-dependent viscosity by a different shear rate.

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1. Introduction

Guar gum is a polysaccharide consisting of a 1,4-linked α -D-mannopyranose backbone with random branches of 1,6-linked β -D-galactopyranose in the ratio of 1.0–1.8:1. Guar solutions have been well studied since the 1980s and have generally been accepted as random coil semi-flexible polymers with high viscosity [1] that arise from the high molecular weight of guar gum and from the presence of extensive intermolecular association (entanglement) through hydrogen bonding [2]. Hence, as a thickening agent, guar gum is extensively used in the food, paper, mining and petroleum industries to modify the rheological properties of functional fluids.

To prepare guar solution for industry, a high amount of freshwater is needed, but water scarcity is one of the most serious global challenges of our time [3]. On the other hand, there are large quantities of seawater around the globe. Utilizing seawater to prepare a guar solution provides financial advantages [4] and alleviates environmental concerns.

Seawater contains natural electrolytes, including cations such as Na^+ , Mg^{2+} , and Ca^{2+} and anions such as Cl^- , and SO_4^{2-} . Due to

the strong electrolyte nature of the applied conditions, the effects of salt on the rheological properties of guar gum have been studied since the 2000s [5–9]. For natural guar gum, a higher apparent viscosity is observed when adding a NaCl/CaCl₂ mixture to a guar gum solution because the shielding of ionic charges formed by salt ions is disrupted, the main chains may be free to expand and hence the viscosity may increase. Considering the concentration of brine reached 20% (w/w) in one study, an increased density helped provide a higher viscosity to the guar gum solution [10]. However, a less entangled state of guar solutions was observed upon the addition of sodium chloride through dynamic oscillatory measurements, indicating a reduced polymer solubility in the presence of salt [7].

The rheological behavior of polysaccharides reflects the ordered conformation usually adopted in solution and the consequent intermolecular interactions [11]. When there are strong interactions between the guar gum molecular chains, the solution of guar gum can block flow channels through underground rock formations and transport sand in artificially created underground fractures. Guar derivatives, such as hydroxypropyl guar (HPG) and carboxymethyl guar (CMG), cover a wide range of industrial applications due to their modified hydration and viscosifying properties compared to natural guar, but the effect of salts on the rheological properties remains unexplored. Because hydroxypropyl group substitution

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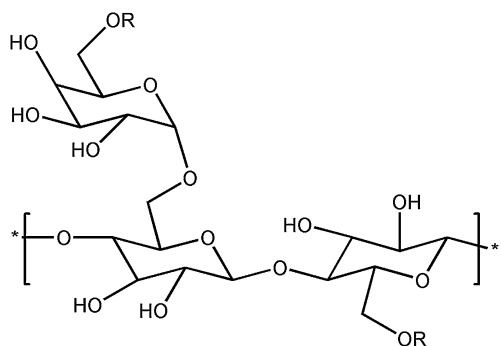


Fig. 1. The structure of the repeating unit of guar gum and its derivatives: R=H for guar gum, R=CH₂CH₂CH₂OH for (hydroxypropyl) guar, and R=CH₂COOH for carboxymethyl guar.

tends to decrease attractive hydrogen bonding interactions, the HPG chain is stiffer than the natural guar, which is consistent with its greater steric hindrance [12]. Therefore, the effect of salt on rheological properties is likely to be altered compared to natural guar. The structure of the repeating unit of guar gum and its derivatives is shown in Fig. 1.

For polyelectrolytes such as CMG and carboxymethyl hydroxypropyl guar (CMHPG), the effect of salt on polymer structure and solution rheology is more complicated. According to the literature, monovalent and bivalent cations produce a screening effect that reduces the segmental repulsions to yield a relatively compact configuration and hence a reduction in the intrinsic viscosity $[\eta]$ of CMHPG, and the effect of bivalent cations has been reported to be greater [6]. Hence, the rheological properties of guar gum and its derivatives are worth further investigation for applications in industry.

This study provides the first investigation of the intrinsic viscosity and rheological properties of GG, HPG and CMG in seawater. Basic structural parameters, such as the intrinsic viscosity $[\eta]$ and the Huggins constant k_H , and rheological parameters, such as zero-shear rate viscosity η_0 , relaxation time λ_0 and flow behavior index n were determined. The effect of parameters of industrial importance, such as concentration, temperature and pH, on these rheological parameters was illustrated.

2. Experimental

2.1. Materials used

The dry powders of guar gum (GG), hydroxypropyl guar (HPG) and carboxymethyl guar (CMG) were purchased from Jiangsu Jingkun Chemical Co. (China). The crude guar gum was purified by a method of the literature mentioned [13]. The average molecular weights M_w for all three samples were determined by Gel Permeation Chromatography (Waters E2695 GPC) and were found to be 2.77×10^6 g/mol for GG, 2.58×10^6 g/mol for HPG, and 2.33×10^6 g/mol for CMG. Seawater was sampled from the East China Sea and was filtered to remove suspended particles. The determination of composition was carried out by ion chromatography (Metrohm 761 Compact IC), and the results were 10985.2, 383.7, 1499.3 and 410 mg/L for Na⁺, K⁺, Mg²⁺ and Ca²⁺, respectively. Deionized water was generated by a Hitech-K flow water purification system.

2.2. Sample preparation

Aqueous solutions of GG, HPG and CMG were prepared by carefully adding the required amount of dry powder into a vortex formed by mixing with a mechanical stirrer continuously for 30 min

at a constant temperature of 25 °C. After stirring, the sample was stored at 25 °C for 4 h for further hydration. Then, the samples were stored at 4 °C to prevent degradation due to bacterial growth. All tests were completed within 24 h after sample preparation.

2.3. Intrinsic viscosity measurement

The intrinsic viscosity $[\eta]$ and Huggins coefficient k_H are vital information on the nature of the polysaccharide in solution, which characterizes the size and interaction of polymer chains. The $[\eta]$ in deionized water can be determined by measuring the viscosity of solutions at low concentrations and extrapolating to an infinite dilution solution, according to the Huggins equation, which was used to obtain the $[\eta]$ of CMHPG in pure water with good correlations [6].

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c, \quad (1)$$

where η_{sp} is the specific viscosity, c is the concentration of polymer solution and k_H is the Huggins coefficient.

The intrinsic viscosity $[\eta]$ in seawater can be determined by Eq. (2) known as Higoiro et al.'s equation, which has been found to determine the $[\eta]$ of aqueous gums solutions in the presence of salt with good correlations [6].

$$\ln \eta_r = [\eta] c, \quad (2)$$

The viscosities of dilute solutions of GG, HPG and CMG were determined using a capillary viscometer (Schott Geräte Ubbelohde Type No. 53110). The temperature of the thermostat was controlled at 25 °C within a range of ± 0.1 °C. The viscometer was calibrated with standard sucrose aqueous solutions. Averages of three repeat experiments were considered for data analysis.

2.4. Steady shear rheological measurements

Rheological property is a characterization of the flow of matter, primarily in a liquid state, which is of great industrial importance. In this paper, rheological property of gum solutions was characterized by steady shear rheological measurements. The rheological testing of the prepared samples was conducted using a rotational rheometer, HAAKE MARS III (Thermo Scientific, Germany). A concentric cylinder with a conical din rotor with a 28-mm diameter, a 42-mm height and a gap of 0.1 mm was used to perform steady-state simple shear for all samples to obtain the shear viscosity as a function of the shear rate at various water bath-controlled temperatures ranging from 20 °C to 50 °C and in concentrations of 0.3%, 0.5%, 0.7% and 0.9% (w/w). The data collection, treatment and regression were performed using the RheoWin 3 (HAAKE) software. Averages of three repeat experiments were considered for data analysis.

3. Results and discussion

3.1. Intrinsic viscosity

The effect of seawater on the reduced viscosities of GG, HPG and CMG was measured at 25 °C. Fig. 2(A) and (B) shows the concentration dependence of the reduced viscosities of gum solutions in deionized water and in seawater respectively. The intrinsic viscosities for GG, HPG, and CMG in deionized water are 11 ± 0.06 , 11.09 ± 0.07 , and 27.52 ± 0.12 dL/g (standard deviation), the corresponding Huggins constant k_H for them are 0.215, 0.556 and 0.104 while the corresponding coefficient of determination are 0.970, 0.957 and 0.971 respectively. The intrinsic viscosities for these three samples in seawater are 12.53 ± 0.13 , 15.38 ± 0.11 and 9.47 ± 0.08 dL/g while the fitting coefficients of determination are 0.998, 0.994 and 0.999 respectively.

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