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A comparative study on viscosity behavior of water-soluble chemically modified guar gum derivatives with different functional lateral groups

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Abstract: A comparative study was carried out on the viscosity behavior of three new water-soluble chemically modified guar gum derivatives with different functional lateral groups, including *O*-carboxymethyl-O-hydroxypropyl guar gum (CMHPG), with anionic character, *O*-2-hydroxy-3-(trimethylammonio)propyl guar gum (HTPG), with cationic character, and *O*-carboxymethyl-*O*-2-hydroxy-3-(trimethylammonio)propyl guar (CMHTPG), with amphoteric character. It was found that the shear rate, concentration, temperature, added salt and surfactant affected the viscosity properties of these new guar gum derivatives in aqueous solutions. Regardless of the functional lateral groups, all sample solutions behaved as non-Newtonian shear-thinning fluids, and their viscosity increased with the increase in their concentration but decreased with the increase in temperature. Aqueous CMHTPG solution had the strongest shear-thinning property, and aqueous CMHPG solution investigated had the greatest viscous flow activation energy. In contrast to cationic HTPG or anionic CMHPG, amphoteric CMHTPG had an enhanced viscosity property in aqueous salt solutions, exhibiting an unusual anti-polyelectrolyte viscosity behavior. The addition of sodium dodecylsulfate was found to result in a decrease in the viscosity of aqueous HTPG solution and an increase in the viscosity of aqueous CMHPG solution or CMHTPG solution.

Keywords: guar gum derivative; functional substitution group; viscosity property; cationic polysaccharide; anionic polysaccharide; amphoteric polysaccharide; aqueous solution

INTRODUCTION

Polysaccharides obtained from different sources and their derivatives with different functional groups are widely used in food systems, where they function as thickeners, stabilizers, gelling agents, texture modifiers, etc. Guar gum, which consists mostly of linear polymannan β-1,4 linked mannose units with single galactose unit side chains, is an important naturally occurring polysaccharide.[1] The chemical structure and high molecular weight of these molecules endow guar gum with a thickening property. Native guar gum can be chemically modified into various water-soluble derivatives by using reactive functional groups to substitute free hydroxyl groups along the macromolecular backbone of guar gum in order to broaden its applications in numerous industries such as food, paints and pigments, oilfield, mining, paper, water treatment, personal care, pharmaceutical and agriculture. In particular, faster and better solubility in water as well as multifunctional characteristics can be obtained for this biomacromolecule by the introduction of ionic substituents. In these cases, viscosity is one of the most important properties and corresponding rheological properties are basic to any function served by the aqueous system containing native or substituted guar gum. Therefore, knowledge of the viscosity behavior of guar gum and its various derivatives in aqueous solutions is essential for meeting end-user requirements.

Some investigations have been undertaken to deal with the viscosity properties of guar gum or its derivatives in solution. Whitcomb *et al.*[2]

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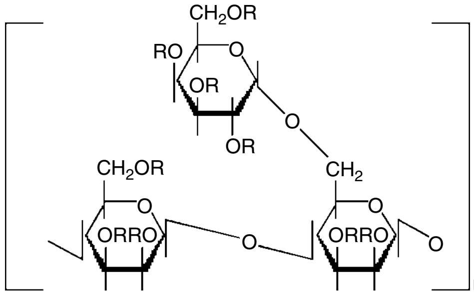
measured the viscosity of aqueous solutions of the galactomannan portion of guar, termed guaran, over a wide range of shear rates and concentrations; Venkataiah and Mahadevan[3] obtained the viscosity characteristics of aqueous solutions of guar gum and its hydroxypropyl and sodium carboxymethyl derivatives by the characterization of their flow properties in the range of low to moderately high shear rates, using a very simple technique and instrument; Casas *et al.*[4] investigated the viscosity properties of diluted solutions of guar gum and its mixture with xanthan; Cheng *et al.*[5] carried out the study of aqueous solutions of guar galactomannan and hydroxypropyl guars with different molar substitution levels using dilute solution viscometry and gel permeation chromatography; Oblonsek *et al.*[6] studied the viscosity properties of carboxymethyl guar gum derivatives with different substitution levels at different concentrations and temperatures, as well as the effects of nonionic surfactants; Lapasin *et al.*[7] dealt with the viscosity changes under continuous shear flow conditions of aqueous systems of hydroxypropyl guar gum (HPG) and three derivatives, of the same or lower molecular weight as HPG, characterized by different contents of long-chain hydrophobic pendants. All these studies showed that the viscosity properties of guar gum and its derivatives were influenced by many factors such as substituents, concentration, temperature, shear rate and added salt and surfactant. Especially for substituted guar gums, the type and level of substituents could significantly change their viscosity behavior. For example,[3] the zero-shear-rate viscosity (η_0) of hydroxypropyl guar gum is lower for a given concentration than that of unsubstituted guar gum, and the decrease is greater with increasing molar substitution of hydroxypropyl groups. At lower concentrations, however, the η_0 value of sodium carboxymethyl guar gum is higher than the unsubstituted guar gum, and at higher concentrations the reverse is true.

In this work, a comparative study was carried out for the first time on the viscosity behavior of three new water-soluble chemically modified guar gum derivatives with different ionic lateral groups, including *O*-carboxymethyl-*O*-hydroxypropyl guar gum (CMHPG), with anionic character, *O*-2-hydroxy-3-(trimethylammonio)propyl guar gum (HTPG), with cationic character, and *O*-carboxymethyl-*O*-2-hydroxy-3-(trimethylammonio)propyl guar gum (CMHTPG), with amphoteric character. These novel polysaccharide-based polyelectrolytes have been used as new additives for food and other systems in China because of their multifunctional characteristics to emulsify, stabilize, flocculate, suspend or form gels when they are used as thickeners. Special emphasis in this study was given to the influence of the charge character of the substituents on the viscosity properties of these guar gum derivatives in aqueous solutions under different conditions of shear rate, concentration, temperature, added salt and surfactant.

MATERIALS AND METHODS

The three water-soluble chemically modified guar derivatives with different functional lateral groups, including anionic CMHPG, cationic HTPG and amphoteric CMHTPG, are commercial products and were kindly provided by the China Agent Office of Economy Polymers and Chemicals Company of the USA (Guangzhou, China). Their repeating unit structures are illustrated in Fig 1. The carboxyl group contents of CMHPG and CMHTPG were obtained from UV analyses at a corresponding maximum adsorption of 204 nm with the help of an ARLAN CARY (Germany) 100-type UV–visible spectrophotometer, and the quaternary ammonium group contents of HTPG and CMHTPG were obtained from nitrogen elemental analyses using an Elementar (Germany) Vario EL elemental analyzer. Table 1 gives the ionic group contents of these products and some other information. For amphoteric CMHTPG, its isoelectric point (IEP) was determined viscometrically to be pH 5.9. The IR spectra of purified CMHPG, HTPG and CMHTPG samples incorporated in KBr tablet, measured on a Bruker (Germany) Vector 22-type FTIR instrument and shown in Fig 2, confirmed the existence of these functional ionic groups. From Fig 2, it was found that the characteristic absorption band of the carboxyl groups at about 1630 cm^{-1}, which is attributed to the C=O stretching vibration of $-COO^-$, appeared in the IR spectra of the CMHPG and CMHTPG samples, and the characteristic peak at about 1110 cm^{-1}, which is attributed to the stretching vibration of C–N bonded with quaternary ammonium groups, appeared in the IR spectra of the HTPG and CMHTPG samples.

The viscosity investigation of three guar gum derivatives in aqueous solutions was conducted with the help of a rheometer (Rheotest 2, 50 Hz, type RV 2; RheoTec Co., Germany) using a cylinder measuring system (S/S_1, 25 mL) under various conditions. The following variables have been studied: shear rate (12 values in the range 3.0–1312 s^{-1}), derivative concentration (three values in the range 0.5–1.5% w/v) and temperature (four values in the range 25–60 °C).



HTPG: R = H or $CH_2CH(OH)CH_2N^+(CH_3)_3$
CMHPG: R = H, $CH_2COOH(CH_2COO\text{-})$ or $CH_2CH(OH)CH_3$
CMHTPG: R = H, $CH_2COOH(CH_2COO\text{-})$ or $CH_2CH(OH)CH_2N^+(CH_3)_3$

Figure 1. The chemical structures of three water-soluble chemically modified guar derivatives with different functional lateral groups.

Table 1. Three new water-soluble chemically modified guar derivatives used in this study

Items	CMHPG	HTPG	CMHTPG
Trade mark	ECOPOL-518T	ECOPOL-14S	ECOPOL-AMPHO-S
Nature of ionic groups incorporated	Anionic	Cationic	Amphoteric
−COOH, mol g^{-1}	5.50 × 10^{-3}	—	6.30 × 10^{-3}
−N^{+} (CH$_3$)$_3$Cl^{-}, mol g^{-1}	—	6.60 × 10^{-4}	5.42 × 10^{-4}
Appearance	Yellow powder	Light yellow powder	Yellow powder
pH, 10 mg g^{-1} solution	7.0	7.0	7.0
Moisture, mg g^{-1}	90	80	80
Particle size, % (minimum through US mesh 120)	>90 (minimum through US mesh 120)	100 (minimum through US mesh 100)	100 (minimum through US mesh 100)

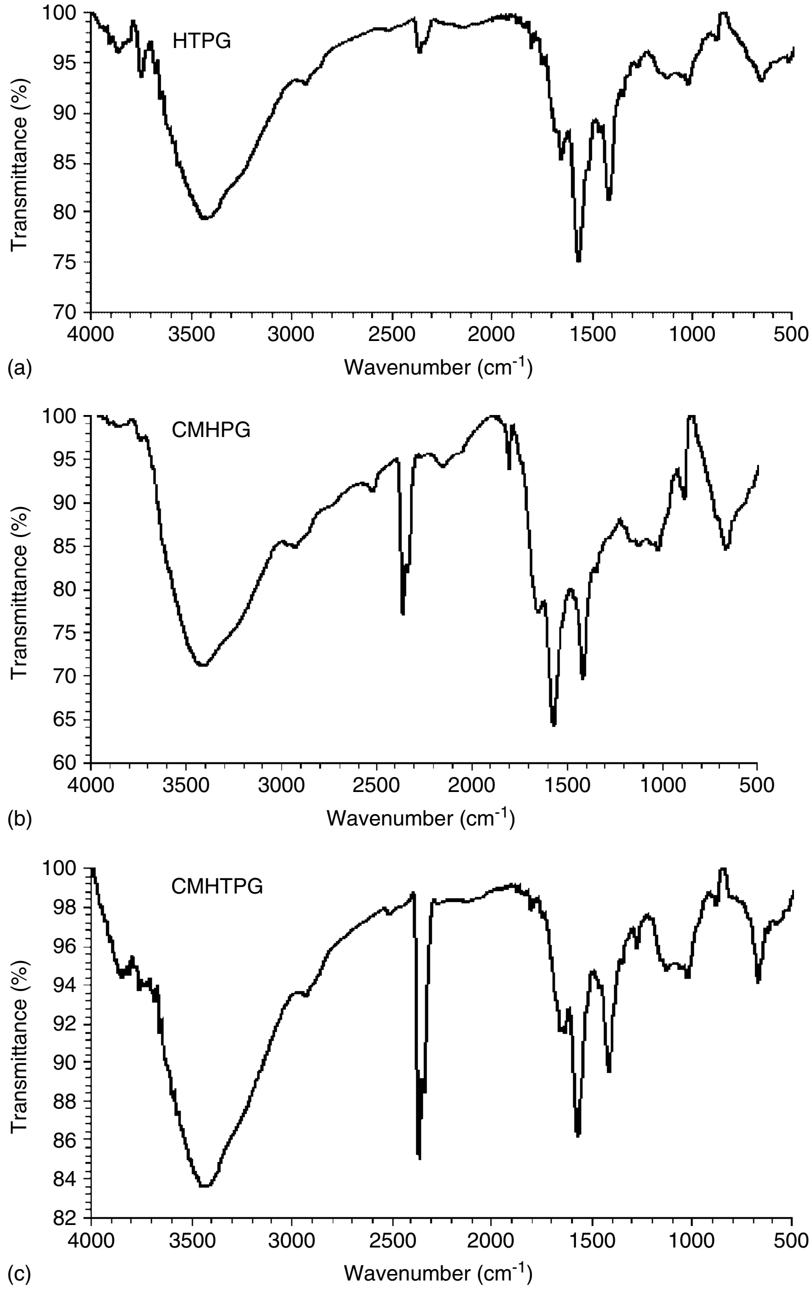


Figure 2. IR spectra of three water-soluble guar gum derivatives with various functional groups. (a) HTPG; (b) CMHPG; (c) CMHTPG.

Moreover, the effects of the added salt (sodium chloride, NaCl) and the surfactant (sodium dodecylsulfate, SDS) on the viscosity properties of the sample solutions were also considered. In all cases, the apparent

Table 2. Flow behavior index (n) and the consistency coefficient (K) for 10 mg g^{-1} aqueous solutions of three water-soluble chemically modified guar gum derivatives, and the corresponding determination coefficient (LRC)

Sample solution	n^a	K^a (mPa s^n)	LRC
CMHPG	0.411 ± 0.019	1920.99 ± 1.09	0.995
HTPG	0.338 ± 0.011	4446.62 ± 1.05	0.998
CMHTPG	0.318 ± 0.008	3936.90 ± 1.08	0.999

[a] Mean ± standard deviation.

viscosity data (η) were calculated from the following equations:

$$\tau = \Phi \times \alpha \quad (1)$$

$$\eta = \tau/\dot{\gamma} \quad (2)$$

where Φ is the cylinder constant, α is the instrument reading, τ is the shear stress and $\dot{\gamma}$ is the shear rate.

RESULTS AND DISCUSSION

Effect of shear rate

The effect of the shear rate on the apparent viscosities of three guar gum derivatives in 10 mg g^{-1} aqueous solutions is given in Fig 3. As seen, the viscosity values of all sample solutions investigated decreased with the increase in the shear rate. The differences in the viscosity are more pronounced at lower shear rates and become less significant at higher shear rates, showing a typical shear-thinning behavior characteristic of non-Newtonian pseudoplastic fluids. When these viscosity curves were plotted in double logarithmic scales, it was found that such plots could give straight lines with good linear regression coefficients (LRC) of more than 0.99, as shown in Table 2. This fact indicates that the pseudoplastic behavior exhibited by aqueous solutions of the guar gum derivative can be well quantified by the following power law relationship:[8]

$$\eta = K\dot{\gamma}^{n-1} \quad (3)$$

where n is the flow behavior index and K is the consistency index. Then, the level of shear thinning for aqueous solutions of the guar gum derivative could be measured by the n value, which decreases when the pseudoplasticity increases. From the results listed in Table 2, lower n values ranging from 0.318 to 0.411 were observed for three derivative solutions, showing their stronger shear-thinning property. In contrast, aqueous solution of CMHTPG incorporating both anionic carboxymethyl and cationic 2-hydroxy-3-(trimethylammonio)propyl substituents has the lowest n value. The result seems to imply that the network structure developed by the interaction between anionic and cationic groups along the CMHTPG chains is broken down under high shear rates more easily than those developed by the interaction from the ionic repulsion of charged groups along anionic CMHPG or cationic HTPG chains. Compared with HTPG, aqueous solution of CMHPG incorporating anionic carboxymethyl and nonionic hydroxypropyl substituents has a higher n value. This may be because the hydrogen-bonding and hydrophobic association actions from the hydroxypropyl substituent of CMHPG reinforce its molecule network structure in aqueous solution, which results in more resistance at higher shear rates.

Effect of derivative concentration

For three guar gum derivatives investigated, the viscosity values of aqueous solutions with three various concentrations, namely 5, 10 and 15 mg g^{-1}, were measured by the rheometer under a shear rate of 5.4 s^{-1} and a temperature of 25 °C. As shown in Fig 4, an increase in the concentration led to an obvious increase in the viscosity. For example, the concentration increase from 5 to 15 mg g^{-1} resulted in corresponding viscosity increases from 138.2 to 2444.8 mPa s for CMHPG, from 318.9 to 5846.3 mPa s for HTPG and from 106.3 to 3933.0 mPa s for CMHTPG. A similar phenomenon was also observed for aqueous solutions of guar gum and locust bean gum.[9,10] According to Casas *et al.*[4] this effect may be due to the molecular chain entanglement of the

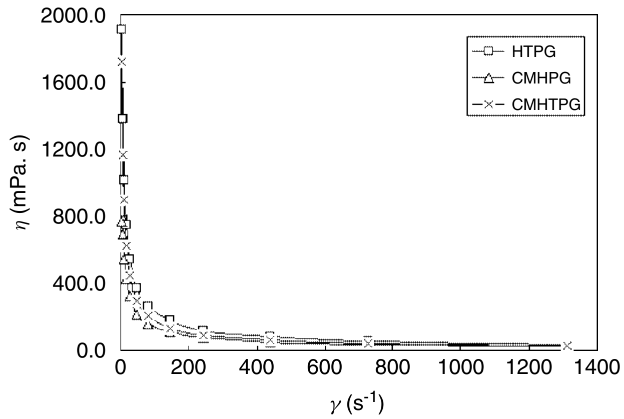


Figure 3. Effect of shear rate ($\dot{\gamma}$) on the apparent viscosity (η) of aqueous solutions of three guar gum derivatives (concentration = 10 mg g^{-1}; pH = 7.0; temperature = 25 °C).

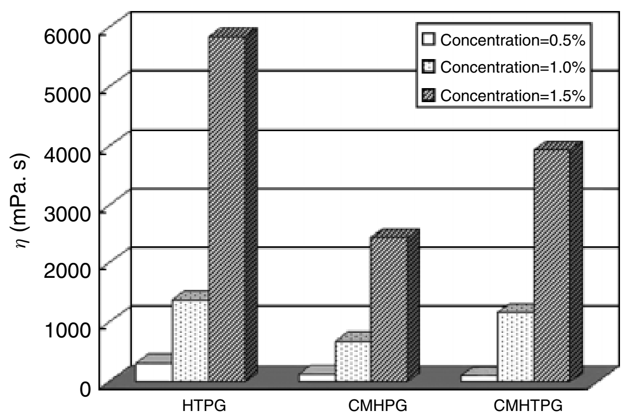


Figure 4. Effect of concentration on the apparent viscosity () for three water-soluble guar derivatives (shear rate = 5.4 s^{-1}; pH = 7.0; temperature = 25 °C).

guar gum derivatives in aqueous solutions. With the increase in concentration of guar gum derivative, the degree of molecular chain entanglement would be enhanced, which results in viscosity increase. In contrast, the viscosity enhancement level of aqueous CMHTPG was greater than that of aqueous HTPG or CMHPG. For instance, the multiplication factor of the viscosity was found to be about 37.0 for amphoteric CMHTPG, 18.3 for cationic HTPG and 17.7 for anionic CMHPG. Similar behavior for the viscosity enhancement was also observed when the derivative concentration increased from 5 to 10 mg g^{-1}. This seems to imply that at higher concentrations amphoteric CMHTPG could form a physical entanglement of the solvated molecular chains for viscosity enhancement by the interactions of oppositely charged substituents more effectively than cationic HTPG or anionic CMHPG by chain expansion due to repulsion of ionic groups.

Effect of temperature

The effect of temperature on the apparent viscosity for 10 mg g^{-1} aqueous solutions of the three guar derivatives was also investigated using the rheometer at a shear rate of 5.4 s^{-1}. It was found that the η values decreased with the increase in temperature for all the example solutions. This effect is caused by the loss of hydration water around the polymer molecules when the temperature increases, which leads to the decrease in viscosity. The plots of ln η vs reciprocal temperature (T^{-1}) are shown in Fig 5. It was found that such plots gave a good linear relationship, which indicates that the extent of temperature effect on the viscosity could be quantified by the following Arrhenius-type equation:[11]

$$\eta = A_0 \exp(E_a/RT) \tag{4}$$

where E_a is the viscous flow activation energy and A_0 is a pre-exponential parameter. Thus, the E_a values reflecting the sensitivity of the derivative solutions to temperature were determined, as shown in Table 3. Among the three derivative solutions investigated, aqueous solution of anionic CMHPG had the greatest E_a value, indicating the greatest sensitivity of the viscosity to temperature.

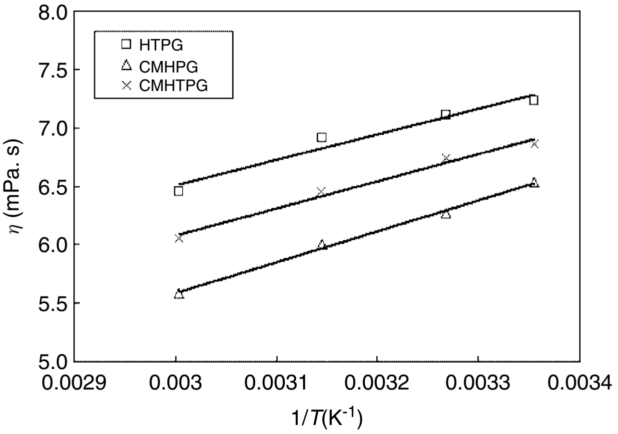


Figure 5. Effect of temperature (T) on the apparent viscosity (η) of aqueous solutions of three guar gum derivatives (concentration = 10 mg g^{-1}; pH = 7.0; shear rate = 5.4 s^{-1}).

Effect of added salt

Figure 6 gives the effect of added salt concentration (C_s) on the apparent viscosities of 10 mg g^{-1} aqueous salt solutions of CMHPG, HTPG and CMHTPG under a shear rate of 5.4 s^{-1}. For anionic CMHPG or cationic HTPG, the viscosity decreased with the increase in added salt concentration, showing a typical ordinary polyelectrolyte behavior. This is because an increase in the salt concentration shields the ionic charges along CMHPG or HTPG chains, which lessens the repulsive forces among the charges and results in the decrease in hydrodynamic volume of the guar gum derivative in aqueous solution. For aqueous salt solution of amphoteric CMHTPG, however, the viscosity increased with the increase in added salt concentration, exhibiting an unusual 'anti-polyelectrolyte' viscosity behavior. This was probably due to the disruption of positive–negative charge attractions resulting from the shielding of the ionic charges along the CMHTPG chain by added NaCl, which allows chain expansion by enhanced solvation. Our previous investigations[12–14] on aqueous salt solutions of other polysaccharide derivatives with amphoteric groups also confirmed such viscosity behavior.

Table 3. Viscous flow activation energy (E_a) and pre-exponential parameter (A_0) for 10 mg g^{-1} aqueous solutions of three water-soluble chemically modified guar gum derivatives, and the corresponding determination coefficient (LRC) (shear rate = 5.4 s^{-1})

Sample solution	E_a (kJ mol^{-1})	A_0	LRC
CMHPG	22.08	0.0921	0.998
HTPG	17.98	1.0214	0.980
CMHTPG	19.41	0.3959	0.992

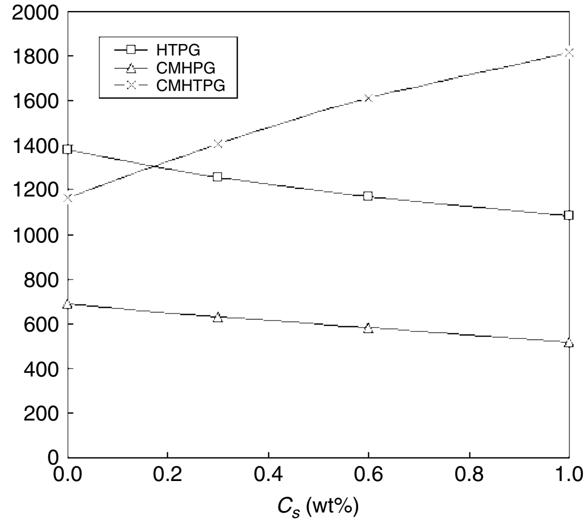


Figure 6. Effect of added salt on the apparent viscosity (η) of aqueous solutions of three guar gum derivatives (concentration = 10 mg g^{-1}; temperature = 25 °C; pH = 7.0; shear rate = 5.4 s^{-1}).

Effect of added surfactant

The influence of SDS on the apparent viscosities of aqueous solutions of three guar gum derivatives at pH 7.0 is given in Fig 7. When the SDS was added in aqueous HTPG solution, a decrease in viscosity was observed. This could mainly be ascribed to the formation of the complex between positively charged HTPG and negatively charged SDS due to the electrostatic attraction. However, the addition of SDS to aqueous solution of CMHTPG or CMHPG led to a viscosity enhancement. This may result from the uncoiling and extension of the CMHPG chain with the negative charge and the CMHTPG chain with net negative charges above its isoelectric point (IEP = 5.9) in the presence of the SDS of the same sign because of the electrostatic repulsions.

CONCLUSIONS

Aqueous solutions of CMHPG, HTPG and CMHTPG behave as typical non-Newtonian shear-thinning fluids with a characteristic flow behavior index lower than 1. Among them, aqueous solution of CMHTPG with amphoteric character has the strongest shear-thinning behavior. Depending on a particular end-use and relevant shear rate range of the application, shear-thinning viscosity behavior might be advantageous owing to the fact that many applications in the food, oilfield and coatings industries need a polymer fluid to exhibit low viscosity when processes such as mixing, pumping or injecting are carried out (corresponding to high shear conditions), and high viscosity when it is stored or put into effect (corresponding to low shear conditions). Moreover, the apparent viscosities of all sample solutions investigated increased with the increase in their concentrations.

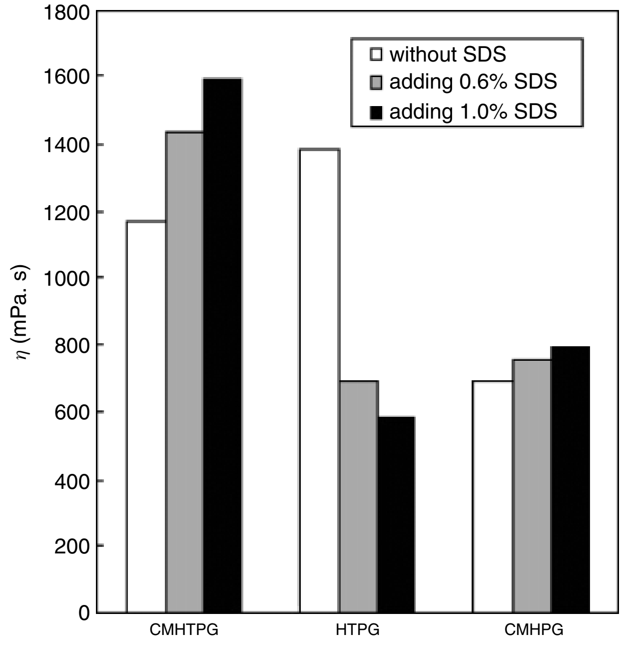


Figure 7. Effect of added surfactant on the apparent viscosity () of aqueous solutions of three guar gum derivatives (concentration = 10 mg g^{-1}; pH = 7.0; shear rate = 5.4 s^{-1}).

The relationship of the apparent viscosity vs temperature for aqueous solutions of three guar gum derivatives studied could be expressed in the form of an Arrhenius-type equation. The activation energy of viscous flow was ordered as follows: CMHPG > CMHTPG > HTPG. In comparison with aqueous HTPG or CMHTPG solutions, aqueous solution of anionic CMHPG has the greatest sensitivity to temperature. From the viewpoint of industrial application, however, the relative thermal insensitivity of the aqueous solution of guar gum derivatives seems to be advantageous.

The effect of added salt on the viscosity property of CMHTPG solution is very different from those observed in salt solutions of HTPG and CMHPG. Anionic CMHPG or cationic HTPG has high viscosity value in water as a result of repulsive interactions of groups with like ionic charges along the macromolecular chains. However, in the presence of added salt, charge–charge repulsions are shielded, resulting in a decrease in viscosity. In contrast to cationic HTPG or anionic CMHPG, amphoteric CMHTPG may display improved viscosity with increased salt concentration of its aqueous solutions due to the addition of salt disrupting the intra- and intermolecular associations, resulting in the expansion of the chain conformation. This unique salt-tolerant property of amphoteric guar gum derivative would be favorable for its use in food and other systems.

In the presence of anionic surfactant, the enhanced viscosity values were observed for aqueous solutions of anionic CMHPG and amphoteric CMHTPG, while a decrease in the viscosity was found for aqueous solution of cationic HTPG under the conditions investigated.

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