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Xanthan and guar polymer solutions for water shut off in high salinity reservoirs

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ABSTRACT

In this research the influence of salt concentration on the rheology of xanthan and guar solutions and their combined mixtures was investigated. Shear viscosity at wide shear rate range was measured for all solutions at various conditions of temperature, polymer concentration, mixing ratio, and salt content. It was found that while xanthan solutions were more susceptible to salt presence in the solutions which has led to reduction in shear viscosity, the viscosity of guar solutions tended to increase upon increasing salt concentration and this was equally pronounced at low and high polymer concentration, i.e. 500 ppm and 3000 ppm. Synergism was not significantly observed for the xanthan/guar mixtures at all ratios used, i.e. 1:1, 1:2, and 2:1. Salt greatly affected the rheology of xanthan/guar mixtures except for mixtures where the guar content was high. We believe that this method, i.e. combining xanthan and guar solutions, is an effective strategy to control rheology and morphology of solutions to be used in enhanced oil recovery field.

1. Introduction

Guar and xanthan are polysaccharides which are extensively used in food industry. The main role of these two polysaccharides is to serve as thickening agents and texture modifiers for food products. The unique characteristic of guar and xanthan gums in terms of rheological properties is that not only they owe significant viscosity values at lower concentrations in aqueous solutions but also they can exhibit excellent synergism when they are mixed together. This feature, i.e. synergistic effect, has drawn much attention in some important applications especially in enhanced oil recovery (EOR) field. Comprehensive overview about chemistry and properties of neat guar and xanthan can be found elsewhere (see Garcia-Ochoa, Santos, Casas, & Gomez, 2000; Heyne & Whistler, 1948; James, 1993; Prabhanjan, Gharia, & Srivastava, 1989). Xanthan is more viscous than guar due to the nature of its chemical structure, i.e. higher molecular weight values. Despite this fact, and as mentioned above, mixtures of guar and xanthan exhibit synergism, i.e. viscosity of mixtures may exceed viscosity of neat gums. This finding had been reported by several studies in the past (Amundarain et al., 2009; Casas, Mohedano, & Garcia-Ochoa, 2000; Fischer, Navarrete, Constien, Coffey, & Asadi, 2001; Khouryieh, Herald, Aramouni, & Alavi, 2006, 2007; Khouryieh, Herald, Aramouni, Bean, & Alavi, 2007; Lopes, Andrade, Milas, & Rinaudo, 1992; Lorenzo, Zaritzky, & Califano, 2008; Mothe, Correia, De Franca, & Riga, 2006; Tako & Nakamura, 1985; Wang, Wang, & Sun, 2002). Virgin xanthan contains acetyl group linked to its backbone which can hinder chain flexibility by forming a stabilized helical ordered structure. For this reason de-acetylated xanthan is more preferable to form mixtures with guar in order to achieve strong synergism. When salt is added to anionic or cationic polysaccharide aqueous solutions, a polyelectrolyte phenomenon may be observed where salt shields the ionic charges along the polymer chains resulting in decrease in repulsion between chains and hence decrease the viscosity (Zatz and Knapp, 2010; Zhang, Zhou, & Hui, 2005a, 2005b). If the shielding of ionic charges formed by salt ions can be disrupted, main chains may be free to expand and hence viscosity may increase (Zhang et al., 2005a). In the open literature, the number of studies that reported the influence of salt on the rheology of guar/xanthan mixtures appeared to be sparse (Fischer et al., 2001; Khouryieh, Herald, Aramouni, & Alavi, 2007; Khouryieh, Herald, Aramouni, Bean, et al., 2007). It has been found by others (Fischer et al., 2001) that addition of up to 2% of KCl to guar/xanthan mixture at 4:1 mixing ration tended to reduce the viscosity of the mixture very significantly. It has also been reported by others that the viscosity of xanthan/guar mixtures increased very rapidly at ratios of 60/40 and 80/20 in fresh water and in the presence of 2 mM of NaCl showing a very strong synergism effect, however in the presence of high salt content, up to 40 mM NaCl, for the same xanthan/guar mixtures no synergism was observed and the overall viscosities were much lower than those with no or low salt concentration (Khouryieh, Herald, Aramouni, & Alavi, 2007; Khouryieh, Herald, Aramouni, Bean, et al., 2007).

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Here one may conclude two things; first: salt can reduce the overall viscosity of the xanthan/guar mixtures, second: synergism may be greatly affected especially at higher salt concentrations. The objective of the present study was to investigate influence of salt in form of combined NaCl and $CaCl_2$ on the steady state flow behavior of xanthan/guar mixtures at various conditions of concentrations and temperatures. The data obtained by current study is anticipated to be very important for the enhanced oil recovery in Saudi reservoirs which are designated by high salinity nature.

2. Experimental

2.1. Materials used

Xanthan and guar were purchased from Sigma–Aldrich Co. Salts used to form brine solutions were sodium chloride (NaCl) and calcium chloride ($CaCl_2$).

2.2. Sample preparation

Aqueous solutions of xanthan, guar, and the mixtures were prepared by mixing with distilled water at concentration of 500–3000 ppm with 500 ppm increment. Brine samples were prepared by mixing fresh samples with 10% (in mass to volume) of NaCl and $CaCl_2$ at a ratio of 80/20 wt%. The mixture ratios used in this study were 1:1, 1:2, and 2:1 xanthan to guar.

2.3. Rheological tests

Rheological testing of the prepared samples was conducted by using rotational rheometer type AR-G2 manufactured by TA, Instrument. Concentric cylinder having a conical din rotor of 28 mm diameter and 42 mm height was used to perform steady state simple shear for all samples to obtain shear viscosity versus shear rate at various temperatures starting from 25 °C to 65 °C with 10 °C increment.

2.4. Displacement experiments

To test the effectiveness of polymer solutions in shutting off excessive water production, single phase displacement runs were conducted using Benthimer sandstone core samples characterized with homogeneous petro-physical characteristics and uniform pore size distribution. The rock samples were 1.5 in. diameter, 3 in. long cylindrical cores with very close permeability and porosity.

Displacement runs were conducted using a Core Flooding Unit Model CFS 830. The runs started by saturating the core sample by placing a dry core sample in a desiccator where vacuum was applied. When appropriate vacuum pressure was reached, the sample was saturated with the brine solution. The weight of the dry core and that of the sample when saturated was used to determine the sample porosity utilizing the saturating fluid density. The fully saturated core sample was then placed in the core holder where confining pressure of 2000 psi was applied. Back pressure regulator was set at atmospheric pressure and oven temperature at 65 °C. When the whole unit reached the desired temperature, brine was injected at different flow rates and pressure drop, when stabilized, was recorded. Darcy law was used to determine sample liquid permeability. After that polymer solution was injected through the core sample at slow flow rate of 1 cm^3/min corresponding to shear rate of 18 s^{-1} and rising pressure drop across the core sample was continuously recorded. The injection continued until full adsorption was achieved as stated by stabilized constant pressure drop. After that pump was switched on to allow the flow to the brine accumulator and brine solution was displaced through the sample rock to flush the non-adsorbed polymer. Pressure drop at this stage started to decline and when pressure drop stabilized the experiment was stopped and the sample was removed out of the core holder and left to dry at room temperature.

3. Results and discussions

Figs. 1 and 2 show shear viscosity versus shear rate for guar and xanthan non-brine solutions at various polymer concentrations tested at different temperatures. As anticipated, xanthan solutions exhibit higher viscosity values in comparison with those of guar solutions, however guar behaves as Newtonian material at relatively lower concentrations (i.e. at 1000 ppm) as seen in Fig. 1. In Figs. 3 and 4, we can observe the influence of brine concentration on the shear viscosity of guar and xanthan solutions. One can notice, as seen in Fig. 3, that increasing brine concentration up to 20% tends to significantly increase guar viscosity. In contrary, Fig. 4 shows that the presence of brine in xanthan solutions is seen to reduce the viscosity to great extent. Hence, one may conclude that ion shielding by brine is associated with xanthan solutions, while in the guar solutions the shielding is disrupted. This is in

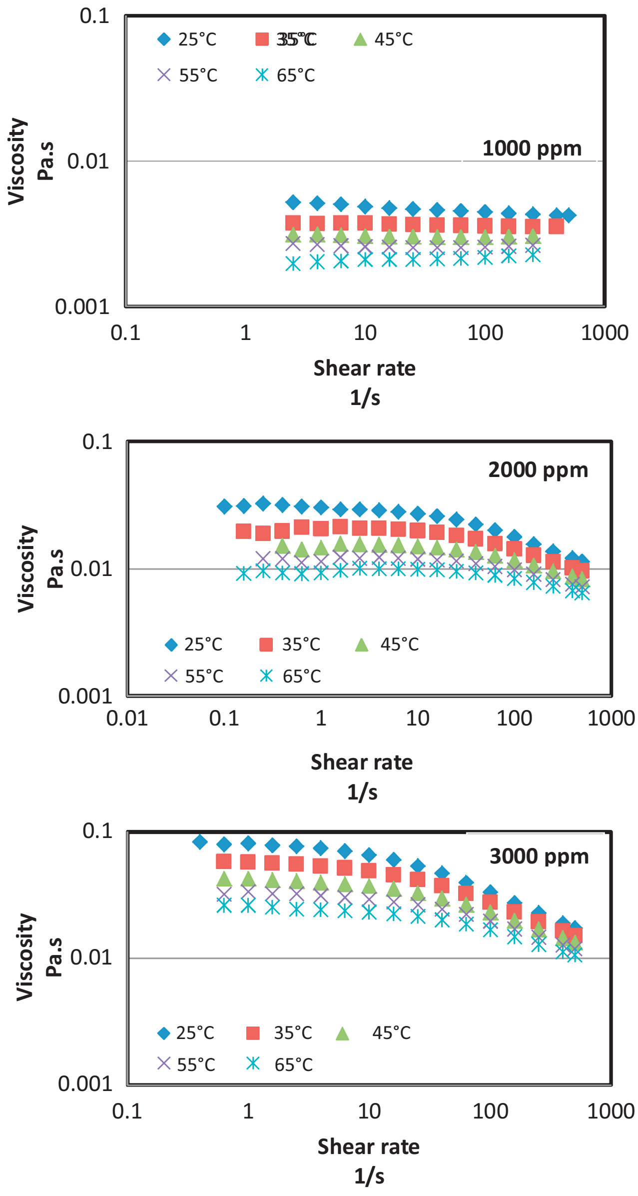

Fig. 1. Shear flow profile for non-brine guar solutions at various concentrations.

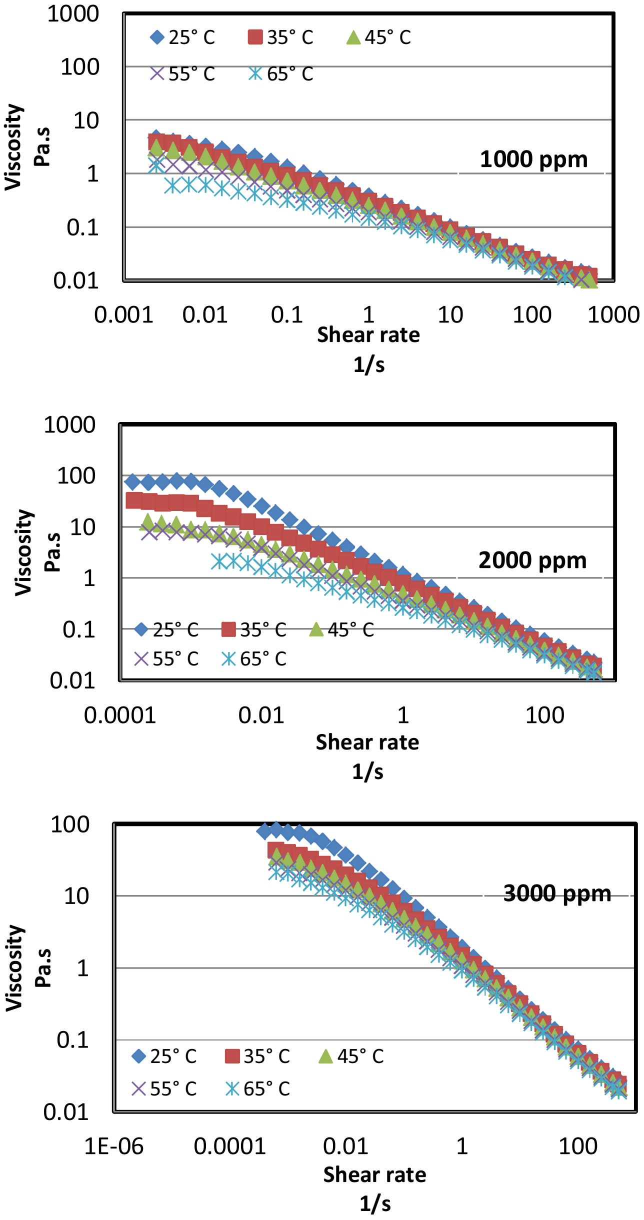

Fig. 2. Shear flow profile for non-brine xanthan solutions at various concentrations.

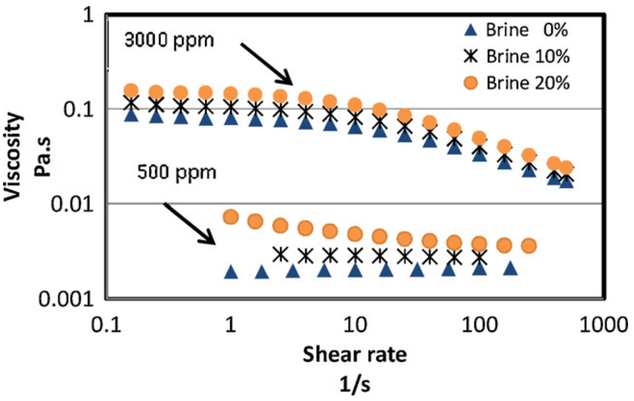

Fig. 3. Effect of brine concentration on the rheology of guar solutions at two concentrations of guar ($T = 25\,^{\circ}\mathrm{C}$).

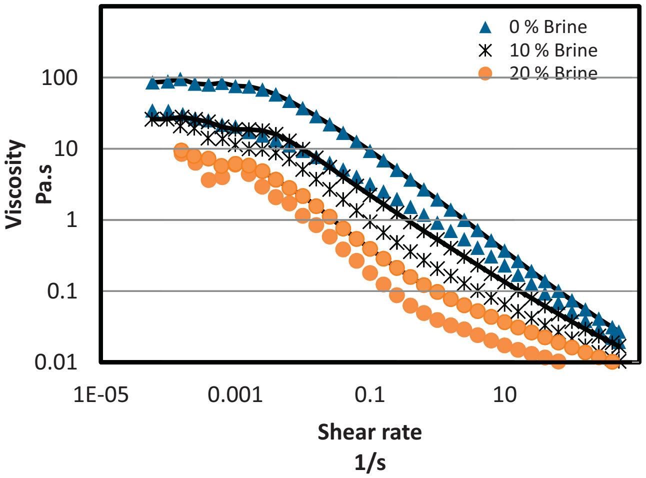

Fig. 4. Effect of brine concentration on the rheology of xanthan solutions at concentration of 3000 ppm measured at 25 °C and 65 °C (solid lines at $T = 25\,^{\circ}\mathrm{C}$).

agreement with data found in the literature (Zatz & Knapp, 2010; Zhang et al., 2005a, 2005b). The rheology of fresh guar and xanthan mixtures with no salt added is presented in Figs. 5 and 6. This data was measured at two extremes of temperature and concentration. It can be seen from Fig. 5 that at lower temperature, i.e. 25 °C, synergism is only prevailed but not at a significant degree at higher polymer concentration, i.e. 3000 ppm, while at lower polymer concentration, i.e. 500 ppm, no synergism was observed, however when xanthan percent increased in the solution viscosity of the mixture increased as well. Needless to say that lacking of synergism at lower polymer concentration and less synergism effect at higher

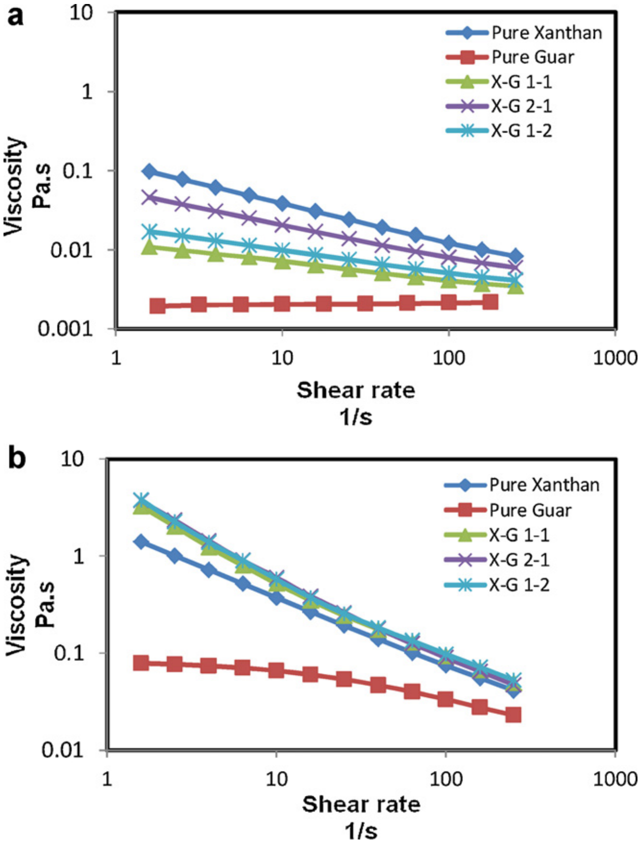

Fig. 5. Rheology of xanthan/guar mixtures at 25 °C and 0% brine. (a) Total concentration of mixture = 500 ppm; (b) total concentration of mixture = 3000 ppm.

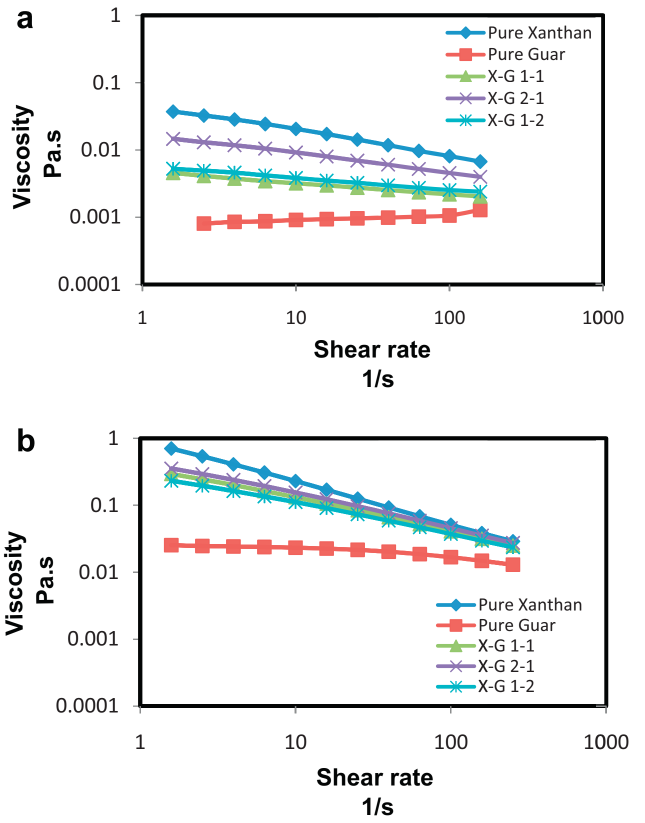

Fig. 6. Rheology of xanthan/guar mixtures at 65 °C and 0% brine. (a) Total concentration of mixture = 500 ppm; (b) total concentration of mixture = 3000 ppm.

polymer concentration may be attributed to the chemical structure of xanthan gum as indicated by FTIR spectrum, not shown here, where acetyl group was detected at a wave-number of 1726 cm^{-1}. At higher temperature, as seen in Fig. 6, no synergism was observed at either the two extremes of polymer concentration. Effect of salt addition on the rheology of xanthan/guar mixtures is plotted in Figs. 7 and 8. One can notice that, from Fig. 7a, at lower polymer concentration while pure guar viscosity increases significantly upon incorporating 20% of salt compared to that of pure guar with no salt added (see Fig. 5), xanthan and xanthan–guar mixtures at all mixing ratios tend to drastically decrease in viscosity. The reduction in viscosity upon adding 20% salt to xanthan and xanthan–guar mixtures is clearly seen at higher polymer concentration, i.e. 3000 ppm, as shown in Fig. 7b. The mixture of 1:2 xanthan to guar has higher viscosity than that of pure xanthan and this is due to higher content of guar in the mixture. One may also realize that at lower shear rate values and when xanthan ratio in the mixture is high inverse-synergism is observed, that is viscosity of mixture is lower than those of pure polymers. Similar behavior was observed at higher temperature as shown in Fig. 8.

Polymer adsorption in petroleum reservoir is desirable to some extent, since it reduces the area open to flow and hence reduces water permeability, thus improving the mobility ratio and increasing oil production. Polymer adsorption and retention occur when polymer molecules interact with solid surface, adhering to grain surfaces mainly by physical forces such as Vander Waals. Polymer adsorption can be measured dynamically by injecting the polymer solution in a consolidated core sample and measuring polymer concentration in core effluent. Two factors are important to study the polymer adsorption and hence, the efficiency of polymer flooding. The first is the resistance factor (RF) defined as the ratio of water mobility to the polymer solution mobility under equivalent conditions of fluid saturation and temperature. The second factor is the residual resistance factor (RRF) describing the rock resistance to flow of water injected subsequent to the polymer solution. This factor provides a quantitative indication of water permeability reduction which is useful to control water fingering due to water injection after polymer flooding. These two terms may be expressed in the following forms:

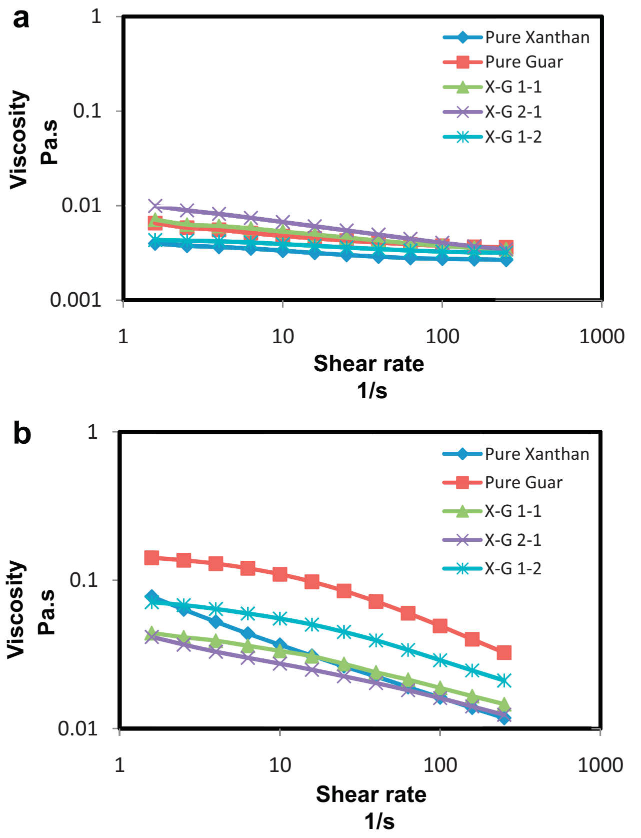

Fig. 7. Effect of brine on the rheology of xanthan/guar mixtures at 25 °C. Brine concentration = 20%. (a) Total concentration of mixture = 500 ppm; (b) total concentration of mixture = 3000 ppm.

$$\mathrm{RF} = \frac{\Delta P(\text{polymer})}{\Delta P(\text{brine before polymer})} \tag{1}$$

$$\mathrm{RRF} = \frac{\Delta P(\text{brine after polymer})}{\Delta P(\text{brine before polymer})} \tag{2}$$

where ΔP is the pressure drop.

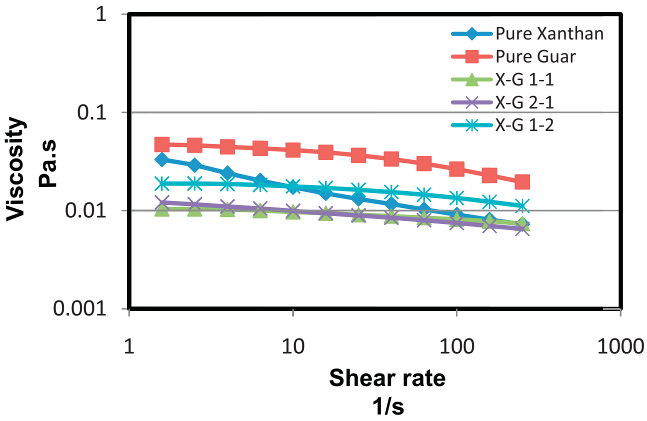

Fig. 8. Effect of brine on the rheology of xanthan/guar mixtures at 65 °C. Brine concentration = 20%; total concentration of mixture = 3000 ppm.

Table 1
Displacement data for xanthan and guar solution at 65 °C and 10% salinity.

Sample no.	Polymer solution (concentration in ppm)	RF	RRF
1	Xanthan (1500)	251.0	165.7
2	Xanthan (3000)	1053.2	601.0
3	Guar (1500)	18.90	17.4
4	Guar (3000)	144.8	91.9

Table 1 shows the displacement data for xanthan and guar solutions measured at 65 °C with 10% salinity and polymer concentration of 1500 and 3000 ppm. Generally, water mobility reduction with polymeric fluids results from both the increase in the adsorbed polymers layer formation at the rock grain surfaces. This behavior is clear in our work when guar and xanthan concentrations were increased from 1500 to 3000 ppm as shown in Table 1. Higher RF and RRF were obtained using xanthan solutions than those obtained using guar solutions at the same concentration. Therefore, xanthan even at low concentration may yield high adsorption on rock surface at the experimental conditions applied yielding favorable properties for water production control. Plugging high permeability pores in reservoir's rocks depends on the relative size of polymer droplet to that of the rock pore. Polymer droplet that is larger than rock's pore size will plug off the pore and hence increase the shut off areas within rock surfaces, and as a result RF and RRF will increase. Here as indicated by Fig. 8, controlling rheology of polymer solution and hence mastering particle size in accordance with rock's pore size may only be achieved by mixing proper ratios of xanthan and guar at same total polymer concentration. In immiscible polymer blends, average particle size is related to concentration and relative viscosity. The merit of current research approach lies on the ability of altering the polymer solution viscosity and hence changing the morphology of the polymer droplet in high saline, and high temperature aqueous environment without the need to increase polymer concentration. For instant shear viscosity of xanthan solution is drastically reduced when the salt concentration is high as indicated by Fig. 8, in this case one may combine xanthan with guar at same total polymer concentration and be able to vary the viscosities of the polymer solution and hence control the particle size that is suitable for shutting off rock's pores.

The elevated value of the residual resistance factor obtained when flooding with low polymers solutions (1500 ppm guar or xanthan) indicates that brine injection that should displace the polymer front through the core samples, did not manage to draw great part of the polymer retained.

4. Concluding remarks

From current research, the following conclusions may be drawn:

- Although xanthan solutions owe higher shear viscosity values compared to those of guars, they are more susceptible to salt which leads to drastic reduction in viscosity.
- Combining xanthan and guar as one mixture offers a practical method to control the viscosity value needed to different applications such as EOR. This is despite the fact that synergism was only observed at high total polymer concentration (i.e. 3000 ppm).
- For EOR in high saline reservoirs such as in the case of Saudi oil reservoirs, one should account for the effect of salt on the rheology of xanthan/guar mixtures as they are greatly affected by the presence of salt, however when the guar content in the mixtures is high; this can compensate for the reduction in viscosity of the solutions. In other words, if xanthan or guar solutions to be individually used for EOR in high salinity reservoirs as shutting off medium for high water permeability zones, one may control the rheology of the solution and hence provide proper particle size that is suitable to plugging the rock's pore by combining xanthan with guar without the need to alter the total polymer solution concentration.

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