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Effect of hydrophobic modification on the structure and rheology of aqueous and brine solutions of scleroglucan polymer

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Abstract−Amphiphilic scleroglucans were synthesized by grafting hydrophobic stearate groups in various densities onto the polysaccharide under its triple-helix conformation. Furthermore, a polyelectrolyte was obtained by attaching ionic-sulfonic groups to the hydrophobically modified scleroglucan. Rheological measurements demonstrated the role of grafted stearates in helix-coil transition of scleroglucan and in reducing the viscosity of scleroglucan in pure aqueous and brine solutions. Nevertheless, grafting the ionic-sulfonic groups caused a substantial recovery of the lost viscosity, especially in brine solution at 90 °C, while keeping the amphiphilic character of the hydrophobically modified scleroglucan. Additionally, the hydrophobic modification altered the adsorption behavior of scleroglucan on oil-reservoir rock surfaces: the higher the grafting density, the greater the adsorption amount. However, the polyelectrolyte sample showed the lowest adsorption among all modified samples. Finally, the modified scleroglucans are promising candidates for enhanced oil recovery applications.

Keywords: Scleroglucan Derivatives, Hydrophobic Modification, Conformation, Rheological Properties, Enhanced Oil Recovery

INTRODUCTION

The past three decades have witnessed the formation of water-soluble hydrophobically modified (HM) polysaccharides in order to create highly accessible, low cost, biocompatible and biodegradable materials as thickening agents and rheology modifiers in many applications such as paints, cosmetics, foods, oil recovery and drug delivery [1-3]. The performance of HM polymers in such applications depends mainly on the degree of the intra- and/or intermolecular associations between the hydrophobic moieties [4]. Although there are many investigations regarding the hydrophobic modification of simple and linear polysaccharides such as cellulose [5], chitosan [6] and pullulan [7], very few studies have focused on more complex, branched polysaccharides such as xanthan or scleroglucan. The former polysaccharides are characterized by their coil conformations in solutions, while the latter ones adopt rigid multiple-helix structures in solutions which can be converted to disordered, flexible coil states depending on the temperature, pH and/or ionic strength of the solutions [8].

Scleroglucan is a neutral β-1,3-β-1, 6-glucan produced by fungi of the genus Sclerotium. This polysaccharide adopts a triple helical conformation in the solid state [9] and exists in a stiff, triple stranded helical structure, when dissolved in water [10].

There are a few examples of modified scleroglucan polysaccharide in the literature [1,11-13]. In addition, to the best of our knowledge, all the reported reactions on scleroglucan have been mainly performed under strongly aqueous basic conditions, where it exists as disordered, flexible coils, and only for drug delivery purposes. On the other hand, scleroglucan aqueous solutions possess interesting and very well recognized rheological properties due to its high molecular weight and stiff helical structure [8]. Actually, aqueous solutions of scleroglucan show high as well as stable viscosities over a wide range of temperature (up to 100 °C/60 min) and pH (0-13) [14]. They also offer high salt and hardness tolerance, low sensitivity to mechanical degradation, and enhanced shear thinning behavior at high shear rates [15].

These unique properties make scleroglucan a highly attractive candidate for industrial applications, especially for enhanced oil recovery (EOR) by polymer flooding. In fact, the good viscosifying ability of the polymer can assure the high viscosity of the injected water and thus low mobility ratio of water to oil, which would finally result in higher sweep efficiency and oil recovery [16,17]. Meanwhile, surfactants are used to lower the interfacial tension between crude oil and formation water as well as to alter wetting properties [17,18]. However, there are some drawbacks associated with the use of both surfactant and polymer, such as high cost and complexity of the proper formulation. In recent years, the synthesis of the so-called polymeric surfactants has been suggested as a promising strategy to simultaneously improve the mobility ratio and reduce the interfacial tension by injection of only one chemical during polymer flooding [19].

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In this work, we present the hydrophobic modification of hydrophilic scleroglucan polymer by grafting alkyl moieties, with variable grafting densities, onto the polysaccharide chains under its helix structure. The above hydrophobic modification would produce polymeric surfactants having simultaneously high viscosifying capacity and ability to lower the water surface tension and thus potential for application in EOR. This also allows us to infer the possible influences of chemical modifications on the conformational features of scleroglucan. The effects of the chemical modifications on the structure and rheological properties of the samples, in both pure aqueous and brine solutions, at low (25 °C) and high (90 °C) temperatures, were investigated using rheological analysis. Also, to test the idea that hydrophobic polyelectrolytes can be more efficient in producing high viscosity than hydrophobically non-ionic analogues [5], anionic sulfonic groups (SO_3^-) were grafted onto the hydrophobically-modified scleroglucan and the properties of the resultant ionic-hydrophobic sample were studied.

Moreover, to explore further the potential of the prepared samples in oil recovery applications, the preliminary adsorption behavior of the pristine as well as modified scleroglucans, from their pure aqueous and brine solutions, onto carbonate rock particles of oil-reservoirs was investigated. The results demonstrate the promising properties of the modified scleroglucans in different oil production processes.

EXPERIMENTAL

1. Materials

Scleroglucan (Sclg, Actigum CS11) with $M_w=8\times10^5$ g mol^{-1} was supplied by Cargill (Germany). Stearoyl chloride (StCl, 97%), and taurine (2-aminoethanesulfonic acid, 99%) were purchased from Sigma-Aldrich and Samchun, respectively. Dimethylformamide (DMF, 99.8%), 4-(Dimethylamino)pyridine (DMAP, 99%), monochloroacetic acid ($ClCH_2CO_2H$, 99%), sodium hydroxide (NaOH), methanol and isopropyl alcohol were obtained from Merck.

Carbonate particles, obtained from one of Iran's oil-reservoir fields, with a mesh size of 16 mm, were used as solid phase in adsorption measurements. Their detailed properties are presented elsewhere [20].

2. Synthesis of Hydrophobically-modified as well as Ionic-hydrophobic Scleroglucans

To synthesize hydrophobically modified scleroglucan, a homogeneous solution of scleroglucan (0.3 g) in DMF (40 ml) was prepared at 120 °C and cooled to 80 °C. Then, 0.2 g of DMAP and different amounts of stearoyl chloride (0.1, 0.3, 0.5 or 0.7 mL) were added to the solution and stirred for 1 h at 80 °C, followed by stirring for 24 h at room temperature. The final products, StCl(x)-Sclg, where x denotes the above-mentioned amounts of stearoyl chloride, were precipitated by methanol and then dried in an oven overnight at 40 °C under vacuum before analysis. Product yields as determined from the weight of recovered scleroglucan products were 76%, 79%, 80% and 82% for StCl(0.1)-Sclg, StCl(0.3)-Sclg, StCl(0.5)-Sclg and StCl(0.7)-Sclg, respectively.

Also, the ionic-hydrophobic scleroglucan was synthesized by grafting taurine molecules onto the prepared StCl(0.3)-Sclg sample. At first, 0.2 g of StCl(0.3)-Sclg was added into 20 mL of isopropyl alcohol containing 1 mL of NaOH (10 M) and a homogeneous solution was obtained by stirring the mixture for 1 h at room temperature. Then, monochloroacetic acid (0.05 g) was added to this solution and the mixture was stirred for 3 h at 50 °C to obtain the carboxymethylated sample, StCl(0.3)-Sclg-CM. Afterwards, 0.7 g of taurine was dissolved for 18 h at 90 °C in 15 mL of an aqueous solution containing 1.5% (w/v) of StCl(0.3)-Sclg-CM. Finally, 0.7 mL of NaOH (10 M) was poured into the solution to obtain StCl(0.3)-Sclg-SO_3^-. The prepared ionic-hydrophobic sample was precipitated by methanol and then dried in an oven overnight at 40 °C under vacuum before analysis. The yield of the StCl(0.3)-Sclg-SO_3^- sample was 70%.

3. Characterization Methods

Fourier transform infrared (FTIR) spectrometry was used to verify the grafting of stearoyl chloride and taurine onto the scleroglucan. Measurements were taken on a PerkinElmer (version 10.03.06) spectrophotometer. The samples were prepared in tablet form by mixing KBr powder and milled synthesized products.

For nuclear magnetic resonance (^{1}H-NMR) spectroscopy measurements, a Bruker 400 MHz spectrophotometer was used. The samples were dissolved in D_2O and the obtained solutions were used for analysis.

4. Intrinsic Viscosity Measurements

The intrinsic viscosities [η] of pure aqueous as well as brine solutions of scleroglucan and the modified samples were determined by an Ubbelohde capillary viscometer (capillary diameter 0.6 mm) at 25 °C and were calculated using Eq. (1) [21]:

$$[\eta]=[2(\eta_{sp}-\ln\eta_r)]^{1/2}/C \quad (1)$$

where η_r is the relative viscosity, calculated by $\eta_r=t/t_0$; η_{sp} is the specific viscosity, calculated by $\eta_{sp}=\eta_r-1$; [η] is the intrinsic viscosity (dL g^{-1}) and C is the initial concentration of sample solution (0.02 g dL^{-1}). The brine solutions were prepared by dissolving the scleroglucan based polymers in an oil-reservoir brine sample with the composition given in Table 1.

5. Rheological Properties

The rheological behavior of the samples was monitored by using a concentric cylinder Physica MCR 501 rheometer (Anton Paar, Austria) equipped with a Peltier device for temperature control. To do the rheological tests, the system was first heated to the desired temperature (25 or 90 °C), and then the prepared solutions were introduced into the heated cylinder and subjected to steady shear or frequency sweep tests. Rheoplus software, associated with the instrument, was used for recording and analyzing the flow behavior

Table 1. Composition of the oil-reservoir brine sample (total dissolved solid, TDS)

	Ions concentration (mg L^{-1})										
TDS	Al	Li	PO_4^{3-}	HCO_3^-	K^+	NO_3^-	Mg^{2+}	SO_4^{2-}	Ca^{2+}	Na^+	Cl^-
12900	1<	1.1	11.1	22	28	49.8	213	266	790	3960	7300

data. Required samples (containing 0.3% (w/v) of the polymers) were prepared by gradual addition of the powdered polymer to the pure water and brine solutions while stirring for four days to obtain viscous solutions.

6. Surface Tension Measurements

The drop weight method [22], was used to determine surface tension (σ) of aqueous solutions of scleroglucan and the modified scleroglucans at 25 °C. The surface tension (σ) was calculated with the following equation:

$$\sigma = \sigma_{H_2O} \cdot \frac{m}{m_{H_2O}} \quad (2)$$

where, σ_{H_2O}, m_{H_2O} and m are surface tension of water (0.072 N m^{-1} at 25 °C [23]), mass of 10 drops of distilled water and mass of 10 drops of aqueous solutions containing different amounts of Sclg, StCl(x)-Sclg or StCl(0.3)-Sclg-SO_3^-, respectively. A four-digit digital balance was used to determine the mass of the drops collected in a glass beaker.

7. Adsorption Experiments

The adsorbent (0.05 g carbonate particles) was added into 10 mL pure aqueous or brine solutions of Sclg and modified Sclgs. The samples were immersed in a water bath at 25 °C or 90 °C and were stirred slowly for a contact time of 24 h. Their contents were then isolated by centrifugation for 15 min at 4,000 rpm. The adsorption process was assessed by determining the residual concentration of polymer in the sample solution using an UV visible spectrophotometer (Optizen 3220 UV) at λ_{max}=317 nm. A series of standard solutions with known polymer concentrations were prepared, and the absorbance of each solution was used to prepare a calibration curve showing how the experimental absorbance varies versus concentration [20]. The absorbance of each centrifuged solution was measured after adsorption at the same wavelength, and the equilibrium concentration was calculated using the calibration curve. The polymer adsorption of adsorbent q_e (mg g^{-1}) was calculated using the following mass balance equation:

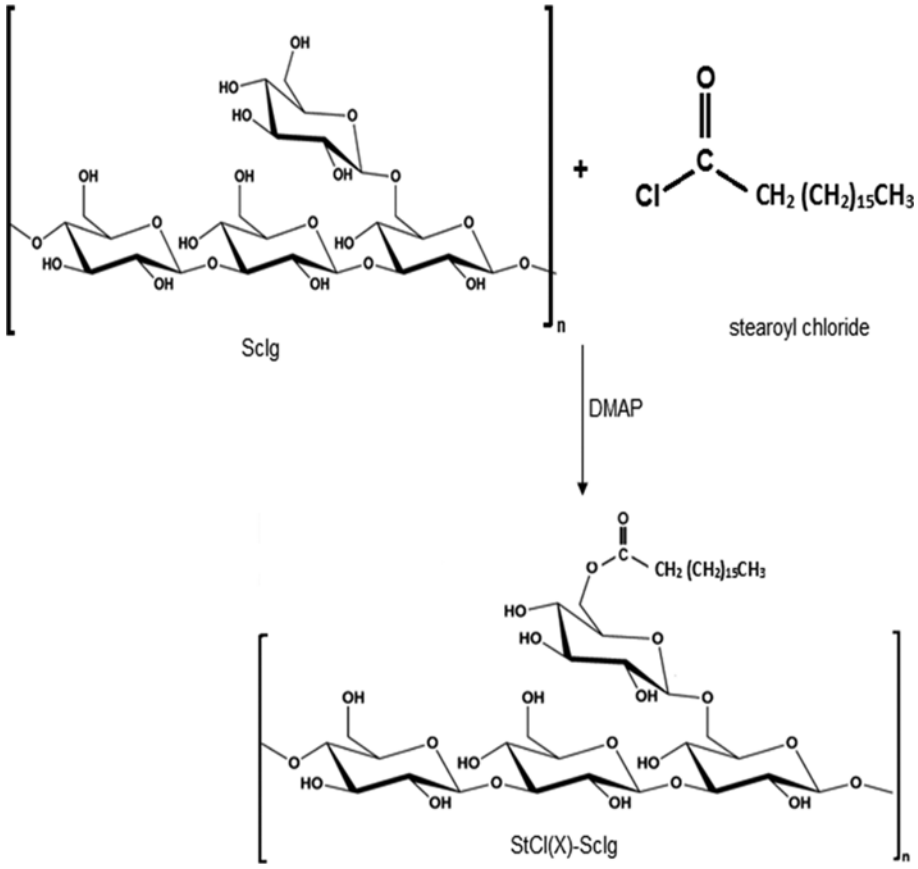
$$q_e = (C_i - C_e)\frac{V}{W} \quad (3)$$

where C_i (mg L^{-1}) and C_e (mg L^{-1}) denote the initial and equilibrium concentrations of polymer, respectively, V (L) is the volume of the solution and W (g) is the mass of the adsorbent used.

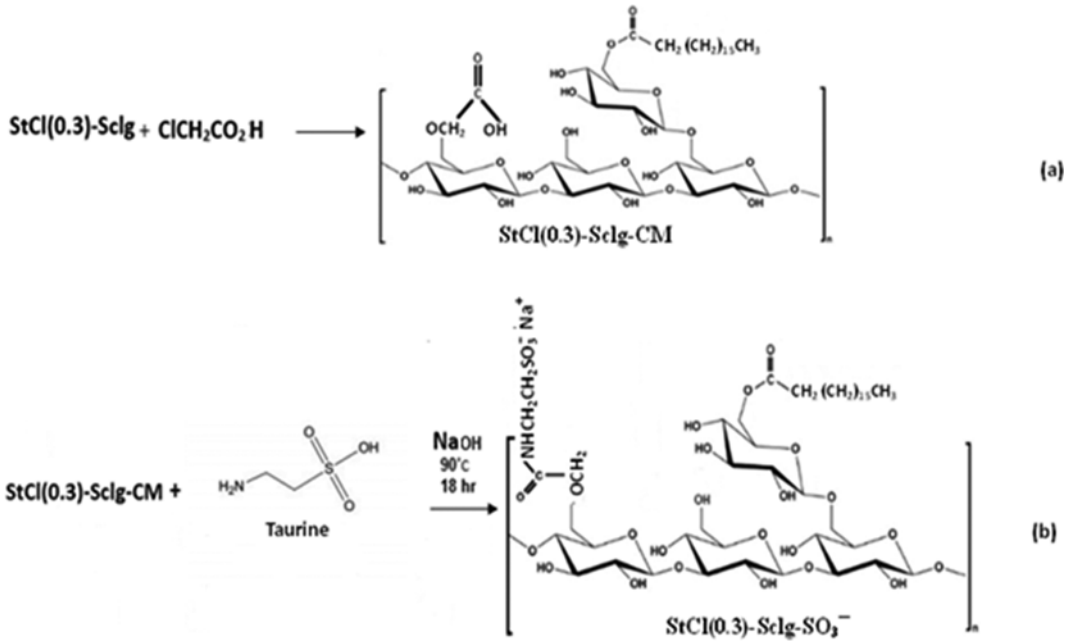
RESULTS AND DISCUSSION

1. Chemical Modification of Scleroglucan

Esterification reactions were used to prepare alkyl derivatives of scleroglucan. The procedure consisted of reacting the polysaccharide with various amounts of stearoyl chloride in the presence of DMAP as a catalyzer (Scheme 1). Due to its high nucleophilic character, DMAP attacks the stearoyl chloride rapidly, forming a highly electrophilic stearoyl-pyridinium intermediate [24,25]. The resultant intermediate subsequently reacts with the hydroxyl groups of



Scheme 1. Synthesis of hydrophobically-modified scleroglucans.



Scheme 2. Synthesis of the ionic-hydrophobic scleroglucan.

scleroglucan to give the ester.

The preparation of the ionic-hydrophobic sample involves first the carboxymethylation of the StCl(0.3)-Sclg sample (Scheme 2(a)). Carboxymethylation of polysaccharides with chloroacetic acid in aqueous solutions, at pH>13, is a well-documented reaction [26]. This reaction will result in conversion of primary hydroxyl groups of the StCl(0.3)-Sclg sample into carboxymethyl groups [27]. Finally, StCl(0.3)-Sclg-SO_3^- sample is synthesized through an amidation reaction between carboxylic functions of StCl(0.3)-Sclg-CM and amine groups of taurine molecules (Scheme 2(b)) [28].

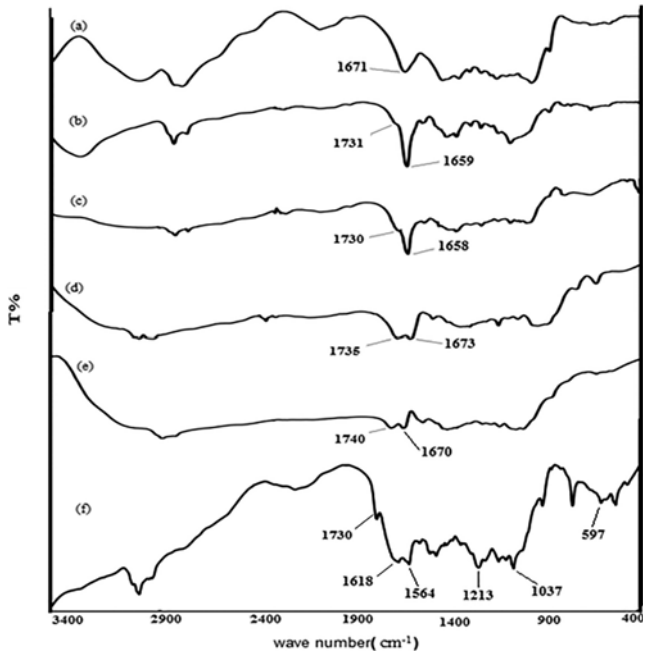


Fig. 1. FTIR spectra of (a) Sclg, (b) StCl(0.1)-Sclg, (c) StCl(0.3)-Sclg, (d) StCl(0.5)-Sclg, (e) StCl(0.7)-Sclg, (f) StCl(0.3)-Sclg-SO_3^-.

Fig. 1 shows FTIR spectra of scleroglucan and different modified scleroglucans. The appearance of new characteristic absorption bands at 1,730-1,740 cm^{-1} in the spectra of modified polymers is attributed to the formation of carbonyl group of ester linkage, confirming the grafting of stearoyl chloride onto the scleroglucan. It is seen that the intensity of carbonyl group peaks was increased by increasing the concentration of stearoyl chloride used in the course of hydrophobic modification. Also, the FTIR spectrum of the ionic-hydrophobic sample, StCl(0.3)-Sclg-SO_3^-, exhibits additional peaks at 1,564 cm^{-1} and 597 cm^{-1} corresponding to bending vibrations of N-H and S-O bands respectively, and also at 1,037 cm^{-1} and 1,213 cm^{-1} corresponding to S=O group duo to the grafted taurine molecules.

The grafting density of the different modified polymers was determined by ^{1}H-NMR. Fig. 2 exhibits the NMR spectra of the pristine scleroglucan, StCl(0.3)-Sclg and StCl(0.3)-Sclg-SO_3^-. NMR spectra of other hydrophobically modified scleroglucans are provided in Supporting Information. For the pristine sample, the peak observed at 4.11 ppm can be ascribed to anomeric protons, and the peaks at 3.58 ppm and 3.74 ppm are characteristic of the methylene protons connected to OH groups on the backbone and those connected to the side chain of scleroglucan, respectively. There are additional peaks in the spectrum of StCl(0.3)-Sclg corresponding to protons on methylene (2.117, 1.841, 1.163 and 1.436 ppm) and methyl (0.737 ppm) groups of the grafted stearate chain. The degree of substitution by the stearate groups (G%) was calculated by comparing the integral of the peak of the methyl protons of the alkyl group (around 0.7 ppm) with that of the peak of anomeric protons (around 4 ppm) using the following Eq. [5]:

$$G\% = \frac{(\text{methyl protons integral})/3}{(\text{anomeric proton integral})} \times 100 \quad (4)$$

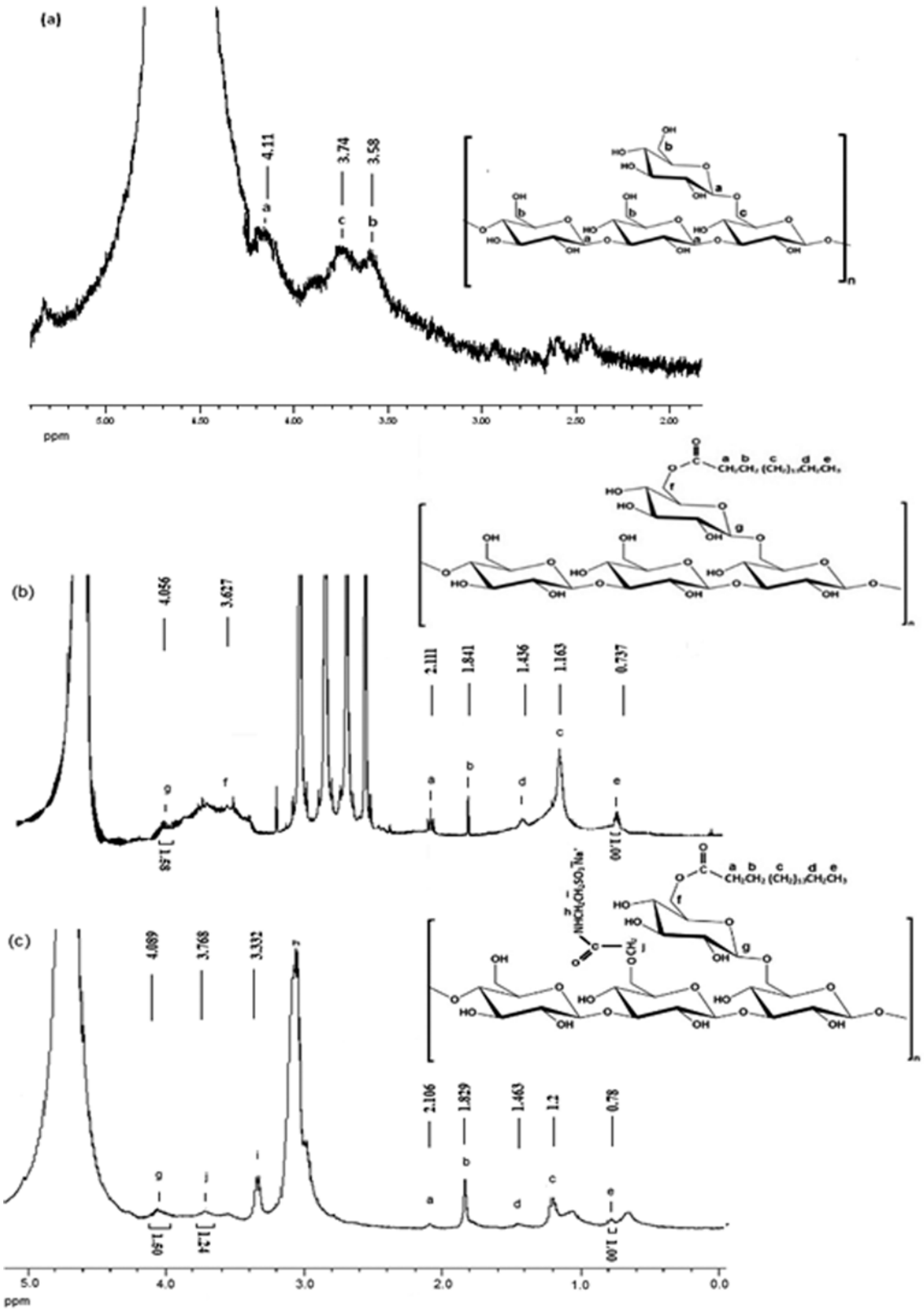


Fig. 2. ^{1}HNMR spectra of (a) Sclg, (b) StCl(0.3)-Sclg, (c) StCl(0.3)-Sclg-SO_3^-.

Accordingly, the grafting densities of StCl(0.1)-Sclg, StCl(0.3)-Sclg, StCl(0.5)-Sclg and StCl(0.7)-Sclg were obtained as 11%, 21%, 29% and 39%, respectively. Despite the high grafting density, all the hydrophobically modified scleroglucans were still water-soluble, but their solubilities were decreased. Thus, a longer time is required for the modified samples to reach complete solubility in water.

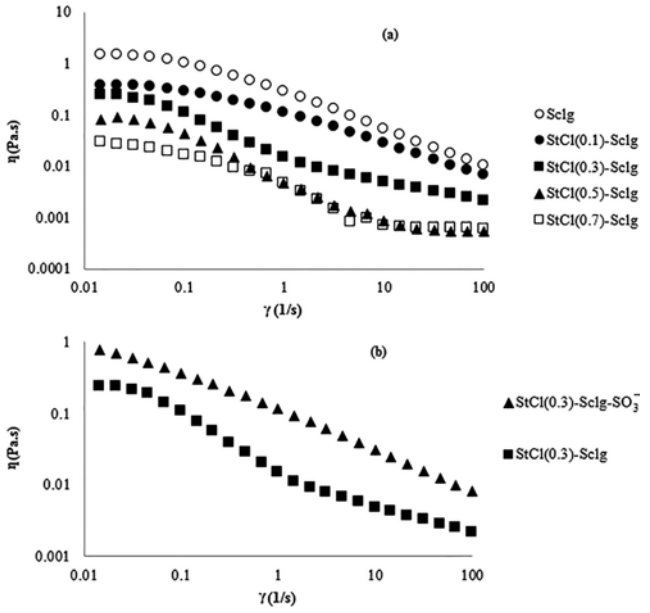


Fig. 3. Viscosity versus shear rate for non-brine solutions of pristine and modified Sclgs, measured at 25 °C.

The NMR spectrum of the ionic-hydrophobic sample, Fig. 2, demonstrates two peaks due to the chemical shifts of protons on methylene groups of the grafted taurine. The peak corresponding to methylene protons connected to nitrogen atom (N-CH_2) appears at 3.056 ppm, while that corresponding to methylene protons connected to sulfur atom (S-CH_2) appears at 3.322 ppm. The peak observed at 3.768 ppm is assigned to methylene protons of the carboxymethyl moiety.

The degree of substitution by the sulfonic group (G_t%) in the hydrophobically modified scleroglucan was obtained as 33% by comparing the integral of the methylene protons peak of the carboxymethyl moiety with those of the peaks of anomeric protons and methyl protons of the alkyl group:

$$G_t\% = \frac{(\text{methyl protons integral})/2}{(\text{methyl protons integral})/3 + (\text{anomeric proton integral})} \times 100 \quad (5)$$

2. Rheological Properties of Pristine and Modified Scleroglucans

Rheological behaviors of all the scleroglucan solutions, shear viscosity (η) versus shear rate (γ), at different measurement conditions are shown in Figs. 3-7. Table 2 shows the consistency coefficients (K) and the flow behavior indexes (n), derived by fitting the viscosity data to the Ostwald-de-Waele model:

$$\eta = K \cdot \gamma^{(n-1)} \quad (6)$$

Plots of shear stress (τ) versus shear rate (γ) for all the samples at different conditions are in Supporting Information (Figs S4-S6).

Fig. 3(a) shows shear viscosity (η) versus shear rate (γ) for non-brine solutions of pristine scleroglucan and hydrophobically modified scleroglucans, measured at 25 °C. The samples showed non-Newtonian pseudoplastic behaviors. Unmodified scleroglucan had the highest viscosity and K value at all shear rates, and the viscosity decreased by increasing the degree of modification. The high viscosity of scleroglucan is mainly attributed to its triple and stiff helical structure, originating from the interstrand H-bonds inside the helical core [8]. On the other hand, we believe that the stearate groups grafted onto scleroglucan weakened the interchain H-bonds, resulting in the viscosity reduction. Moreover, investigating the dilute solution viscometry data (intrinsic viscosity, [η], Table 3) reasonably explains that grafting could additionally affect the conformation of scleroglucan. As seen, scleroglucan showed an [η] value of 21 dL g^{-1} in pure aqueous solution at 25 °C, corresponding to the triple helix conformation [29], while [η] values of hydrophobically-modified scleroglucans were significantly lower than that of the scleroglucan, pointing to their coil-like and single strand conformations [29]. Previous studies [30,31] have shown that some solvents can dissociate scleroglucan triplex into random coils, due to the chaotropic solvent properties. Therefore, to determine any potential chaotropic effect that could arise due to the DMF solvent,

Table 3. Intrinsic viscosity of scleroglucan and modified scleroglucans at 25 °C

Sample	[η] dL/g	
	Aqueous solution	Brine solution
Sclg	21.00	17.52
StCl(0.1)-Sclg	14.05	9.02
StCl(0.3)-Sclg	3.81	3.57
StCl(0.5)-Sclg	3.41	3.04
StCl(0.7)-Sclg	3.29	2.42
StCl(0.3)-Sclg-SO_3^-	18.80	16.20

Table 2. Consistency coefficients (K) and flow behavior indexes (n) for scleroglucan and modified scleroglucans in aqueous and brine solutions

Sample	Aqueous solution 25 °C		Brine solution 25 °C		Brine solution 90 °C	
	K (mPa·S^n)	n	K (mPa·S^n)	n	K (mPa·S^n)	n
Sclg	275.1	0.29	203.0	0.33	148.0	0.42
StCl(0.1)-Sclg	107.2	0.4	46.4	0.5	98.1	0.36
StCl(0.3)-Sclg	15.0	0.44	10.1	0.52	26.5	0.30
StCl(0.5)-Sclg	5.5	0.39	4.5	0.4	20.5	0.14
StCl(0.7)-Sclg	3.8	0.46	3.6	0.53	8.4	0.31
StCl(0.3)-Sclg-SO_3^-	113.0	0.42	61.3	0.49	119.0	0.35

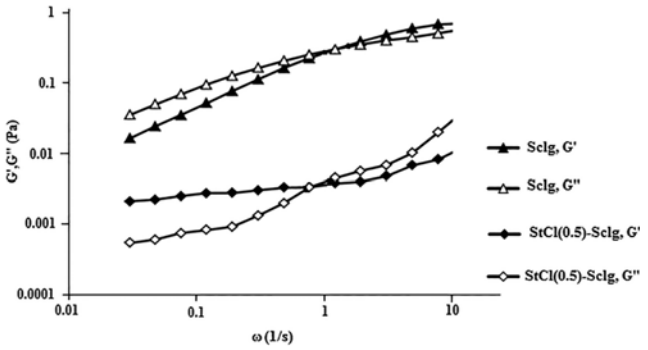


Fig. 4. Frequency dependence of storage and loss modulus of aqueous solutions of Sclg and StCl(0.5)-Sclg, measured at 25 °C (the solid lines are guides to eye).

the pristine scleroglucan was first dissolved in DMF, then precipitated by methanol, and finally was used for preparation of an aqueous solution for the intrinsic viscosity measurement. However, the [η] value of 21 for the pristine scleroglucan, Table 3, confirms that DMF solvent had no or very little effect on the triple helix structure of scleroglucan.

A decrease in intrinsic viscosity as the result of grafting hydrophobic moieties onto other glucan polymers, such as dextran, was also reported previously [32]. To further investigate the changes in conformation of scleroglucan due to chemical modification, the frequency dependence of the storage and loss modulus of aqueous solutions of scleroglucan and StCl(0.5)-Sclg samples are shown in Fig. 4. The two moduli cross at ω_{Sclg}=1.2 s^{-1} and $\omega_{mod\,Sclg}$=0.7 s^{-1}, correspond to $\tau_{Sclg}=\omega_{Sclg}^{-1}$=0.8 s and $\tau_{mod\,Sclg}=\omega_{mod\,Sclg}^{-1}$=1.4 s as the relaxation times for pristine and modified scleroglucans, respectively. It is reasonable to conclude that the slower dynamics (higher τ value) of the modified scleroglucan may be due to the increased interamolecular hydrophobic associations of its coil-like chains.

The effect of ionic modification on the viscosity of hydrophobically modified scleroglucan in pure aqueous solution can be observed in Fig. 3(b). The ionic-hydrophobic scleroglucan, StCl(0.3)-Sclg-SO_3^-, shows much higher viscosity and K value than those of its respective hydrophobically modified scleroglucan, StCl(0.3)-Sclg. Also, [η] value of StCl(0.3)-Sclg-SO_3^- in pure water was five times greater than that of the StCl(0.3)-Sclg, Table 3. As mentioned earlier, hydrophobic modification altered conformation of pristine scleroglucan resulting in a decrease in intrinsic viscosity of the polysaccharide. On the other hand, StCl(0.3)-Sclg-SO_3^- has a polyelectrolyte nature and can dissociate in aqueous surroundings into a chain-fixed anion and a mobile counter-ion bearing the opposite charge. On dissolving polyelectrolyte chains, all counterions diffuse away and distribute themselves homogeneously in the solvent. Then, the chains get fully stretched in a reaction to the repulsive forces between the chain-fixed charges [33,34]. Therefore, the high [η] value of StCl(0.3)-Sclg-SO_3^- in water could be due to the repulsion between ionic parts of the ionic-hydrophobic scleroglucan, causing the polymer network to span over a large sample volume.

Fig. 5(a) shows the effect of the high salinity environment on the rheology of unmodified scleroglucan and hydrophobically modified scleroglucans, at 25 °C. Similar to the behaviors in salt-free

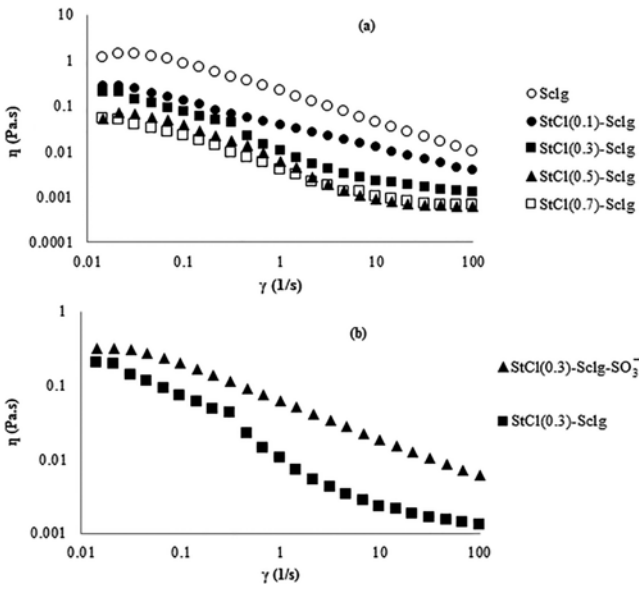


Fig. 5. Viscosity versus shear rate for brine solutions of pristine and modified Sclgs, measured at 25 °C.

solutions, Fig. 3(a), viscosity of scleroglucans decreased by increasing the grafting density in brine solutions. Also, Table 2 demonstrates less pseudoplastic behavior (lower K and higher n values) of scleroglucan and hydrophobically modified scleroglucans in brine solutions compared to those of the different scleroglucans in non-brine solutions, at 25 °C. The observed decrease in viscosity and pseudoplasticity can be attributed to the salting-out effect, causing a reduction of intermolecular interactions and an increase in interamolecular interactions in the presence of salts [8,35]. Moreover, the osmotic effect of salts resulted in preventing the diffusion of more water molecules between the polysaccharide chains, and thus in reducing polymer expansion and shear viscosity [8].

However, investigation of data of Table 2 allows inferring that hydrophobic modification with a grafting density equal to or greater than 29% could make scleroglucan less sensitive to the presence of salts. As can be seen, the consistency coefficient of scleroglucan in pure aqueous solution decreased by 25% with respect to that of scleroglucan in the brine solution at 25 °C. On the other hand, the corresponding K value of StCl(0.5)-Sclg decreased by 18% and that of StCl(0.7)-Sclg remained approximately unchanged. A comparison of the rheological behavior of StCl(0.3)-Sclg and its ionic counterpart in the brine solutions at 25 °C, Fig. 5(b) and Table 2, shows that, as in the case of pure aqueous solutions, the repulsion between ionic parts of the ionic-hydrophobic sample resulted in higher viscosity and K value for StCl(0.3)-Sclg-SO_3^- in the solution containing high salt concentration. As seen in Table 2, K values of StCl(0.3)-Sclg and StCl(0.3)-Sclg-SO_3^- were reduced by 33 and 51%, respectively, as a result of salt addition, at 25 °C, while the respective increases in their n indexes were nearly the same. Hence, it can be concluded that StCl(0.3)-Sclg-SO_3^- was more susceptible to salts than StCl(0.3)-Sclg. This may be ascribed to the shielding of ionic charges along the ionic-hydrophobic chains by salt ions leading to decreases in repulsion between chains and thus in polymer viscosity [36,37]. Thus, the repulsive forces between the

chain-fixed charges of the ionic-hydrophobic sample are screened by counterions such as Na^+, Mg^{2+} and Ca^{2+}, existing in the brine solution, which eventually results in less chain expansion and lower viscosity [34]. On the contrary, the non-ionic StCl(0.3)-Sclg sample was less affected by the salt ions.

The above-mentioned effects of salts also led to decreases in the intrinsic viscosities of the polymers, Table 3. Regarding pristine scleroglucan, we believe that an [η] value of 18 dL g^{-1} suggests the coexistence of triplex and single strand conformations in the brine solution at 25 °C. This hypothesis is corroborated by higher relaxation time of scleroglucan in the brine solution (τ=1.4 s, Fig. 6) with respect to that of scleroglucan in pure aqueous solution (τ=0.4 s, Fig. 6), pointing to the higher intra- and/or intermolecular interactions in the former system.

Fig. 7(a) shows the combined effects of high salinity and elevated temperature (90 °C) on the viscosity of different scleroglucans (pristine and hydrophobically modified). These data are quite informative for assessing the performance of polymer solutions at real oil-reservoir conditions. The samples exhibit the same features as those observed in Figs. 3(a) and 5(a), namely, the reduction of viscosity with increasing the grafting density. Moreover, as shown in Fig. 7(b), the viscosity of the ionic hydrophobic sample, measured at 90 °C in the brine solution, was higher than that of the respective hydrophobic sample at the same conditions. However, in contrast to the pristine scleroglucan, each hydrophobically modified scleroglucan as well as the ionic-hydrophobic scleroglucan showed higher viscosity and larger pseudoplasticity (higher K and lower n values) in brine solutions at 90 °C as compared to those in pure aqueous or brine solutions at 25 °C (see Table 2). This interesting finding signifies the effect of temperature on the enhanced solubility of the hydrophobic moieties of scleroglucans in aqueous solutions, even in the presence of high concentrations of salts.

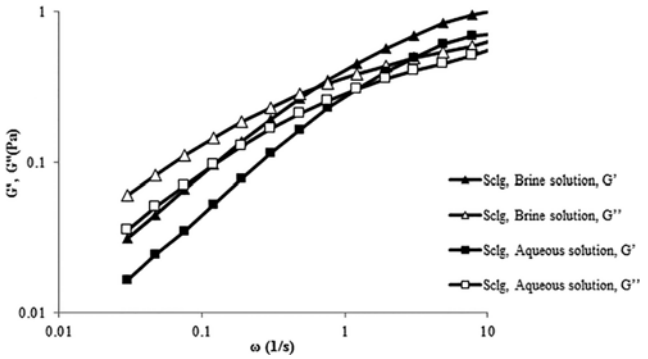


Fig. 6. Frequency dependence of storage and loss modulus of aqueous and brine solutions of Sclg, measured at 25 °C (the solid lines are guides to eye).

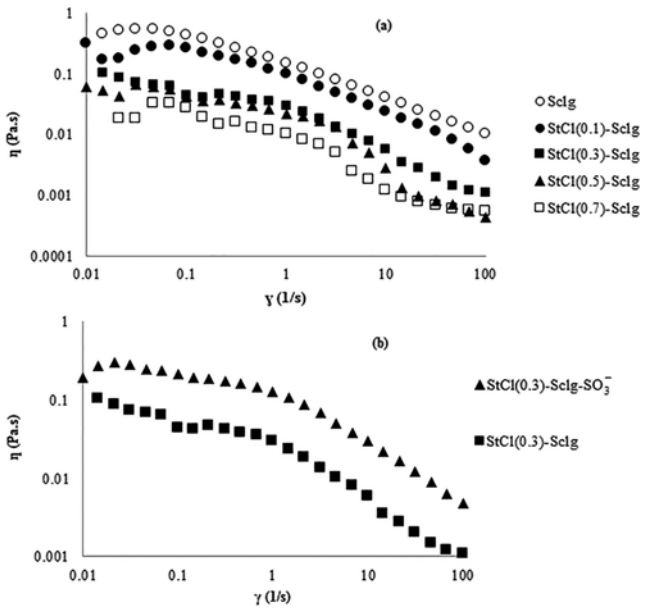


Fig. 7. Viscosity versus shear rate for brine solutions of pristine and modified Sclgs, measured at 90 °C.

3. Quantifying the Hydrophobicity of Modified Scleroglucans

The drop weight method was employed to assess the surface tension of aqueous solutions of scleroglucan and the modified scleroglucans and thus to rank the hydrophobicity of the modified scleroglucans [38]. Lower surface tension (σ) values of polymer aqueous solutions would correspond to more hydrophobicity of the dissolved polymers [39,40]. Fig. 8 shows σ values, calculated by Eq. (1), versus polymer concentration for aqueous solutions of all the studied scleroglucans. Pristine scleroglucan, as a hydrophilic polysaccharide, exhibits the highest surface tension values. On the other hand, as expected, hydrophobicity of scleroglucan was increased by increasing the grafting density. In other words, the grafting strategy renders the hydrophilic polysaccharide into an amphiphilic one. Also, the ionic hydrophobic sample, StCl(0.3)-Sclg-SO_3^-, had nearly the same level of hydrophobicity as that of its hydrophobicallymodified counterpart, StCl(0.3)-Sclg, implying that ionic sulfonic groups did not significantly modify the StCl(0.3)-Sclg/water interactions.

While the pristine scleroglucan, when dissolved in water, causes an apparent increase in the measured surface tension of its aqueous solution, the modified Sclgs, dissolved in water, cause an apparent decrease in the measured surface tension of their solutions. These contrasting results can be explained by the differences in polar intermolecular interactions of the pristine and modified Sclgs [39,41]. The unmodified Sclg contributes strongly to the polar free energy of cohesion through the multiple interactions between their highly

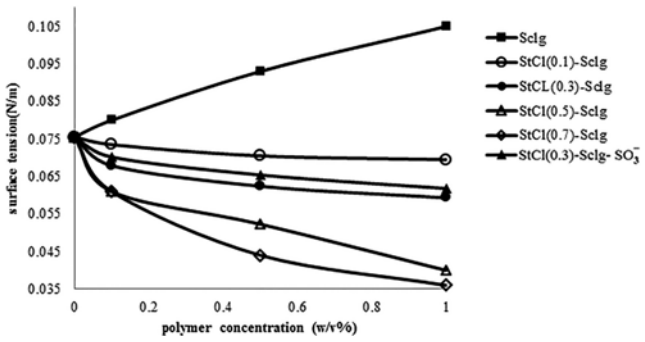


Fig. 8. Surface tension versus polymer concentration for aqueous solutions of all the studied scleroglucans, measured at 25 °C (the solid lines are visual guides).

available hydroxyl groups with the surrounding water dipoles. However, once hydrophobically modified, this polysaccharide loses the strong bipolarity of the Sclg molecules. In fact, hydrogen-bonding attractions that could freely take place between dissolved Sclg molecules are limited in modified polymers to near-neighbor polar interactions on the same chain, without being able to contribute significantly to the cohesion of the liquid [39].

4. Adsorption Measurements

Polymer adsorption on oil-reservoir rock surfaces would affect its performance in oil recovery applications. Optimal adsorption of polymers enhances oil production by reducing the area open to water flow and thus decreasing the water permeability and improving the oil to water mobility ratio. Therefore, investigating the influences of chemical modifications on the adsorption behavior of the samples would be of great importance. The adsorption amount of the pristine and modified scleroglucan samples on carbonate rock particles, at different operational conditions, is represented in Table 4. It is seen that the adsorption amount of hydrophobically-modified scleroglucan is increased by increasing the grafting density. As it mentioned earlier, grafting stearate groups onto scleroglucan changed its stiff triple helix conformation to a more flexible coil-like conformation. The coil-like conformation renders the chains of scleroglucan the possibility to attach to the rock particles by bringing more segments in contact with the surfaces. Multi-layer adsorption caused by hydrophobic interactions [42] could be another reason behind the high adsorption of the hydrophobically-modified scleroglucans.

On the other hand, despite the potential electrostatic attractions between the ionic-hydrophobic sample, StCl(0.3)-Sclg-SO_3^-, and the positively charged carbonate rock surfaces, the sample showed the lowest adsorption amount among the modified scleroglucans at all the conditions tested, Table 4. Stiffer single strands of StCl(0.3)-Sclg-SO_3^-, as revealed by dilute solution viscometry, having less ability to bring their segments in contact with the rock surfaces, may be regarded as the underlying cause for the observed low adsorption amount. The repulsion between ionic parts of an already adsorbed StCl(0.3)-Sclg-SO_3^-, chain and a dissolved one in the solution may be another explanation [43] for the decline in the adsorption of the ionic-hydrophobic sample, compared to those of the hydrophobically-modified scleroglucans.

Investigating the data of Table 4 reveals that the adsorption of the modified samples was increased in the presence of high concentration of salts, due to increased hydrophobic interactions in the brine solution [44]. In addition, the higher adsorption amount of the modified samples in the presence of salts at 90 °C, Table 4, compared to their adsorption amount at 25 °C, can also be ascribed to enhanced solubility and thus higher hydrophobic interactions of the grafted stearate chains at the higher temperature.

Table 4. Adsorption amount (mg g^{-1}) of the pristine and modified Sclgs, from their aqueous and brine solutions, on carbonate rock particles, at 25 and 90 °C

Sample	Aqueous solution		Brine solution	
	25 °C	90 °C	25 °C	90 °C
Sclg	654	710	689	713
StCl(0.1)-Sclg	726	740	810	824
StCl(0.3)-Sclg	804	837	852	883
StCl(0.5)-Sclg	816	841	868	891
StCl(0.7)-Sclg	825	856	875	898
StCl (0.3)-Sclg-SO_3^-	711	733	798	820

In summary, our results demonstrate the potential of modified scleroglucans as promising agents for different processes of oil production, based on the type and extent of the modifications applied. On one hand, the amphiphilic ionic-hydrophobic, StCl(0.3)-Sclg-SO_3^-, polymer possessing appropriate viscosifying properties in brine water at low concentrations and high temperatures which also showed relatively low adsorption on rock surfaces, seems to be a good candidate for polymer flooding purposes. On the other hand, hydrophobically modified scleroglucans, StCl(x)-Sclg, yielding high adsorption on rock surfaces at the experimental conditions applied, would be of interest for permeability alteration and water production control purposes in high salinity and heterogeneous reservoirs [37]. Interestingly, not only the adsorption amount of scleroglucan but also the nature of plugging high permeability pores in reservoir's rocks by this polymer can be tuned via controlling the grafting density. For example, StCl(0.1)-Sclg sample having relatively high intrinsic viscosity (Table 3) and thus consisting of expanded polymer chains would be suitable for plugging pores of large size. However, contracted chains of hydrophobically modified scleroglucans with higher grafting density would plug off the pores of small size more efficiently [37].

CONCLUSIONS

Different hydrophobically modified scleroglucans, with grafting density between 11 and 39%, were prepared by grafting stearate groups onto the polysaccharide under its triple-helix structure. Also, the polyelectrolyte sample, StCl(0.3)-Sclg-SO_3^-, with sulfonic group substitution degree of 33% was obtained by reacting StCl(0.3)-Sclg sample with taurine molecules. According to the rheological investigations of pure aqueous as well as brine solutions of the modified samples at 25 and 90 °C, a helix-coil transition in scleroglucan, as a result of the grafted stearate groups, was suggested. The transition led to a reduction in the viscosity of scleroglucan solutions, due to weakening effects of the grafted groups on interchain H-bonds of pristine scleroglucan. On the other hand, the viscosities of aqueous and brine solutions of StCl(0.3)-Sclg-SO_3^-, at both low and high temperatures, were significantly higher than those of its non-ionic analogue. Moreover, study of adsorption behavior of hydrophobically-modified scleroglucans onto carbonate rock particles revealed an increased adsorption amount as the result of increasing the grafting density. However, the StCl(0.3)-Sclg-SO_3^- sample showed a lower adsorption compared to all the hydrophobically-modified samples. We finally suggest that the modified scleroglucans are potential candidates for a new generation of EOR agents.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/

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