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Colloidal dispersion gels based on sulfonated polyacrylamide and chromium triacetate for harsh-environment

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Abstract−The aim of this study was to outline the preparation of colloidal dispersion gels (CDGs) based on sulfonated polyacrylamide (SPA) and chromium triacetate and investigating their stability in harsh conditions. The effect of crosslinker, polymer concentration, salinity, and gelation time and temperature on the formation, rheological behavior and size distribution of CDGs and also their thermo-chemical stabilities were investigated. It was found that the shear viscosity and size of CDGs decreased with increasing of preparation time. Dynamic light scattering and scanning electron microscopy evaluations showed that the size of CDGs particles decreased with increasing of the Cr^{3+} concentration. In addition, SPA solution had yield stress, while CDGs did not. The elevation of temperature inhibits while the salinity does not disturb the formation of CDGs. In the systems with lower polymer concentration, CDGs were formed. Conversely, in the systems with higher polymer concentration, bulk gels were formed. After aging, CDG sample had a minimal viscosity loss, indicating its exceptional thermo-chemical stability.

Keywords: Colloidal Dispersion Gel, Sulfonated Polyacrylamide, Aging, Yield Stress, Oil Recovery

INTRODUCTION

Polymers and gels have been widely used to improve oil recovery and reduce water in production wells. Two important roles of polymers and gels in the oil field are displacing oil in porous media [1,2] and in-depth profile modification [3,4] which can be regarded as a classification for the polymeric systems used in oil recovery.

Use of bulk *in situ* hydrogels in reservoir is the most common way for in-depth profile modification. However, this method suffers from some serious drawbacks. These gels are formed *in situ*; therefore, the properties of gels depend largely on the physio-chemical conditions (such as temperature, pH, salinity) of the reservoir. Besides, the gel strength as well as the gelation time and location are difficult to predict [5-10]. Although in some studies organic cross-linkers were introduced to obtain *in situ* hydrogels, multivalent cations such as Cr^{3+}, Al^{3+} or Zr^{4+} are common to produce *in situ* hydrogels based on acrylamide polymers [11-13].

On the other hand, it is known that the main problem of polymeric solutions used for displacing oil in porous media is the viscosity loss in the high temperature, salinity and shear stress [14-18]. Some recent studies have addressed the applicability of new classes of polymeric systems such as weak [19], preformed particle [20], micro- [21,22] and colloidal dispersion gels (CDG) [23-27] for both oil displacement and in-depth profile modification which have some advantages over previous commonly used polymeric systems.

CDG is a promising emerging polymeric system which has been given much attention during the last decade because of its remarkable oil recovery properties [23-27]. In general, the CDG system is a weak gel that can be transported through the porous media to modify in-depth profile while it pushes oil out of the reservoir as well. CDG particles can be defined as a dispersed phase of discrete, intra-molecularly crosslinked polymeric gels that are uniformly dispersed in a solvent medium. In general, CDG consist of roughly spherical particles, formed by a crosslinking reaction between crosslinker and polymer. In CDG, the crosslinker coils the polymer and reduces the motional degrees of freedom compared to the pure polymer [28]. As Chang et al. [29] reviewed the progress made in CDG processes in China, including field results, new concepts, and economics, CDGs performed better than polymer flooding, with an incremental recovery efficiency of approximately 14% original oil in place. They also noted that a combination of polymer flooding with CDG would maximize the benefits of both mobility and in-depth profile improvement because a large amount of CDG would preferentially enter the high permeability or thief zones and divert polymer or water into medium and low permeability zones. In addition, they remarked the higher recovery in the CDG process.

In some studies, the laboratory works and field trials involving CDG have been studied. Their results show that CDG injection gives increased oil recovery from laboratory test that has been water flooded to residual oil saturation and from field test. The additional oil recovery is mainly due to increased sweep efficiency and diversion, caused by blocking of pores by CDG particles [23-27]. Some other studies have been conducted in preparation of CDGs and investigation of their rheological behavior and field applications. Most of the studies focused on CDGs based on hydro-

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lyzed polyacrylamide (HPAM) as the polymer and Al^{3+} as the crosslinker [3,30-36].

SPA is a copolymer of acrylamide and sodium salt of acrylamido propyl sulfonic acid. Therefore, it has been thought that the relatively stable SPA polymer can also be used to form CDGs for EOR application. However, there is no report in the open literature on that.

The use of aluminum citrate as the crosslinker may not be without problems. Both ions are pH dependent [35,37,38], which necessitates more controlled preparation conditions. Furthermore, loss of the aluminum to the porous medium is believed to be the major limiting factor [12]. Therefore, in this research, we used another common crosslinker, chromium triacetate, instead. In spite of the carcinogenicity issue of chromium cations especially for Cr^{6+}, chromium triacetate is one of the most widely used inorganic crosslinkers to produce gels with anionic polymers because of its lower toxicity. To the best of our knowledge, there is no report on the preparation and rheological behavior of CDGs based on sulfonated polyacrylamide and chromium triacetate for EOR applications. Also, the use of sulfonated polyacrylamide is not as common as HPAM because it is a functionalized polymer with a narrower range of application. The sulfonated polyacrylamide has higher thermal stability and salt tolerance in oil reservoir conditions than standard hydrolyzed polyacrylamides, and commercially it is used in oil fields applications up to 120 °C. No reports are available discussing the thermal stability of CDG systems in electrolyte media. Therefore, in this research sulfonated polyacrylamide and Cr^{3+} were used for preparation of CDGs. In this regards, a series of SPA/chromium triacetate CDGs were prepared and effects of parameters such as polymer concentrations, crosslinker/polymer ratio and salinity on their flow behaviors as well as their size distribution were studied. In addition, the thermo-chemical aging of SPA solutions and CDG samples was compared.

EXPERIMENTAL STUDIES

1. Materials

SPA with an average molecular weight of 8×10^6 Dalton, sulfonation degree of 25% and water content of less than 10 wt%, was provided by SNF Co., under the trade name of AN125. Chromium triacetate, as a metallic cross-linker, was purchased from Carlo Erba (Italy).

2. Preparation and Characterization of CDG Systems

The CDG systems were prepared according to the following steps. At first, the SPA solutions were prepared by gradual addition of the SPA powder to water (either distilled or saline), while stirring to obtain clear viscous solutions. Aqueous solutions of chromium triacetate were prepared separately and then added to the SPA solution. Then the reaction mixtures (gelant solutions) were stirred at the gelation temperature (Table 1) using a magnetic stirrer at 70 rpm for 24 hrs and left for up to one week at the same temperature to ensure an adequate crosslinking. Table 1 presents the polymeric systems which are classified based on the experiments performed.

The viscoelastic and steady shear flow properties of samples were evaluated using a Physica MCR 501 rheometer (Anton Paar, Austria) equipped with concentric cylinder geometry CC27 (ISO3219) with measuring bob radius 13.33 mm, measuring cup radius 14.46 mm. The gap between the bob and cup of rheometer was equal to 1.13 mm. Rheometer was equipped with a Peltier device for temperature control. For the rheological tests, the system was first heated to the desired temperature, and then the prepared solution was introduced into the cylinder and subjected to shear strain. Rheoplus software was utilized for recording and analyzing of flow behavior data. All the measurements were at 40 °C.

For the thermo-chemical aging tests, the polymeric systems were kept in a suitable container in an oven at 90 °C for 30 days.

Table 1. The test types and details of the SPA/Cr^{3+} polymeric systems

Test type	Output	SPA (ppm)	Cr^{3+}/SPA (W/W)	Gelation temperature °C	Water salinity (ppm)	Gelation time (day)
Viscosity measurements	Viscosity-shear rate (1)	500	0, 1/40, 1/30, 1/20, 1/10	40	0	7
		500	1/20	40	0	1, 3, 5, 7
		1000	0, 1/20, 1/10	40	0	7
		2000	0, 1/20, 1/10	40	0	7
		500	0, 1/20, 1/10	60, 80	0	7
		500	0, 1/20, 1/10	40	1707, 3850, 7700	7
	Viscosity-shear stress	500	0, 1/40, 1/30, 1/20, 1/10	40	0	7
	Viscosity-shear rate (2)*	500	0, 1/20	40	0	7
			0, 1/20, 1/10	40	7700**	7
Characterization test	DLS	500	0, 1/40, 1/30, 1/20, 1/10	40	0	7
		500	1/20	40	0	1, 3, 5, 7
		500	1/20	40	1707, 3850, 7700	7

*This series of tests was performed before and after thermal aging of the polymeric systems at 90 °C for 30 days

**The CDGs were prepared in distilled water for a gelation time of 7 days and then mixed with saline water (for 1 day) to obtain a final salinity of 7700

After 30 days, the steady shear flow properties of these samples was evaluated and compared with the non-aged samples.

Scanning electron microscopy (SEM) studies were carried out using a CamScan MV2300 scanning electron microscope. One or two drops of the SPA solution or CDG systems were placed onto the surface of a clean glass sheet by a dropper, and then dried at room temperature in a dust-free working cabinet. The samples were coated by sputtering a thin gold layer. The samples were observed under high vacuum through an SEM; the accelerating voltage was 15 kV.

Dynamic light scattering measurements were conducted by means of a Malvern NANO-ZS Zetasizer (Malvern Instruments, England) at wavelength λ of 532 nm. The angle for scattering intensity measurements was 173°. All the measurements were at ambient temperature.

RESULTS AND DISCUSSION

1. The Effect of Preparation Time

Two accepted methods are used for probing the rheological characterizations of crosslinked polymeric systems. In the first method, the polymeric systems in liquid state are subjected to steady shear flow and the shear stress is measured and the viscosity is calculated. In the second method, small amplitude oscillatory shear gives the storage modulus (G′) and loss modulus (G″) and damping factor, which show the viscoelastic nature of the gel system [4]. In this research, both methods were used for probing the effects of different parameters on rheological properties. But due to dilute nature our polymeric samples, the small amplitude oscillatory measurements results were not repetitive; therefore, the steady shear tests results were reported.

Fig. 1 shows the effect of preparation time on the viscosity of CDG samples. This figure indicates that the shear viscosities of CDGs kept at 40 °C for several days have small dependency on time and the slight decreasing of viscosity corresponds to further intra-molecular crosslinking reactions in CDGs [35]. The gelation mechanism of SPA-Cr^{3+} can be described by ionic reaction between anionic groups of SPA (including the carboxylate and sulfonated groups) and Cr^{3+} molecules. In low polymer concentrations, most of the crosslink bonds are likely to be intra-molecular. But at high polymer concentrations, intermolecular crosslinking between Cr^{3+} and SPA chains occurs and, consequently, a three-dimensional network forms [34]. The gelation kinetics depended on several factors such as temperature, polymer and crosslinker concentration and salt concentration of gelation media [13]. Due to low concentration of SPA in our samples, it seems that intra-molecular crosslinking reactions occur for our systems and CDGs form after several days. This behavior was confirmed by measuring the Z-average sizes of CDGs particles at different gelation times. It is known that Z-average size is the intensity-weighted mean size derived from the cumulates analysis. The variation of Z-average size during the preparation process of CDG in distilled water at 40 °C is shown in Table 2. The results from Table 2 indicate that when the time passes and preparation process of CDG is progressed, the value of Z-average size of CDGs decreases. Decreasing the Z-average sizes of CDGs might be attributed to the intramolecular association of anionic groups of SPA chain and Cr^{3+} molecules, which induces the shrinkage of molecules. These results are consistent with the viscosity results presented in Fig. 1. On the other hand, progressing of CDG formation process led to decreasing of CDG particles sizes and reducing the viscosity of samples.

2. The Effect of Crosslinker Concentration

The concentration of crosslinker is an important factor on the CDG behavior. To illustrate the effect of crosslinker on flow behavior of the CDG systems, steady shear viscosity measurements were performed on various CDGs, differing by their crosslinker con-

Table 2. Z-average sizes of CDGs particles with 500 ppm SPA and crosslinker/polymer ratio (w/w) of 1/20 as a function of preparation time

Z-average particle size (nm)	Preparation time (days)
4240	1
3830	3
3400	5
2840	7

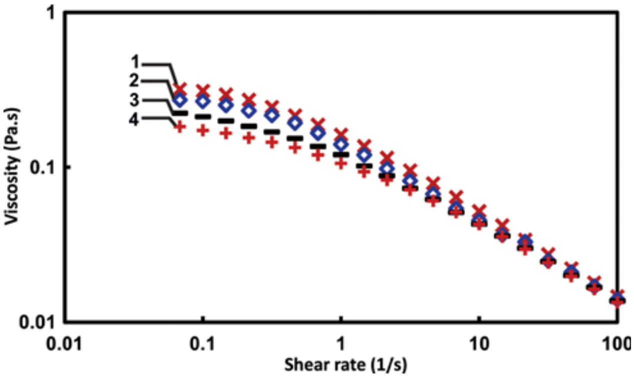

Fig. 1. Viscosity-shear rate behavior for SPA/Cr^{+3} systems prepared in distilled water with respective preparation time (in days) of (1) 1, (2) 3, (3) 5 and (4) 7 (crosslinker/polymer ratio (w/w): 1/20, polymer concentration: 500 ppm, gelation temp.: 40 °C).

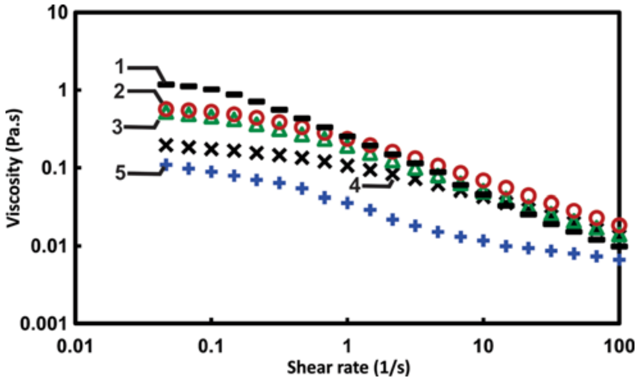

Fig. 2. Viscosity-shear rate behavior for SPA/Cr^{+3} systems prepared in distilled water after 7 days keeping at 40 °C gelation temperature with respective crosslinker/polymer ratio (w/w) of (1) 0, (2) 1/40, (3) 1/30, (4) 1/20 and (5) 1/10 (polymer concentration: 500 ppm).

centration. Fig. 2 shows steady shear viscosity for CDGs with 500 ppm SPA and with different crosslinker/polymer ratio. In this figure the viscosity of samples decreases by increasing of Cr^{3+} content. In CDGs the crosslinker originally forms both intra- and inter-molecular bonds with a preference for intra-molecular bonds [35]. Accordingly, the viscosity decreases due to the dominance of intra-molecular bonds and more collapses of the colloids. It seems that the viscosity of samples at lower shear rates is nearly independent of shear rate. In this regards, the CDGs can be classified as Newtonian fluids at lower shear rates. However, at higher shear rates, the samples behave as a pseudoplastic fluid and shear viscosity continuously decreases with increasing of shear rate; i.e., the shear thinning effect occurred for all samples. This behavior may be due to breakdown of inter-molecular polyacrylamide-chromium bridges in the shear fields and free moving of colloidal particles in solution. However, for CDGs the shear dependence is less than SPA polymer. In CDG systems, the viscosity decreases with increasing of crosslinker concentration, and the shear dependence is less pronounced [35].

For SPA solution, the anionic charges distributed on the polymer molecules would make branch chains to be naturally in curl-state. The curled molecule chains are straightened when the shear stress is acted on [25]. Hence at higher shear rates, SPA polymer has a high shear thinning behavior.

For CDG systems a rheological approach toward the determination of yield stress is provided and the viscosity-shear stress behaviors are evaluated. A number of researchers have conducted comparative studies on yield stress. For a viscosity plot, the yield stress is estimated as the stress at which viscosity just starts to exhibit a rapid drop in value [39]. It can be seen from Fig. 3, that there is a dramatic drop in viscosity plots of SPA solution, which can be interpreted as the yield behavior in this system. For CDG samples their drop in viscosity is not as steep as SPA solution. By increasing of Cr^{3+} content in CDG samples the sudden change in viscosity is faded. According to the fundamental Flory's concept and well-known direct experimental evidences, polymer solutions are treated as statistically structureless. Meanwhile, there are many examples of structure formation in polymer solutions proven by direct optical and/or spectral methods as well as manifested in their macro-properties (including rheological properties) [40]. The yield stress of SPA solution demonstrates that physical entanglements of SPA chains form very weak network structures. Increasing of Cr^{3+} content in CDG causes intra-molecularly crosslink points to increase, CDG size to decrease and CDG particles to disperse more in solution; therefore, network structure is not formed.

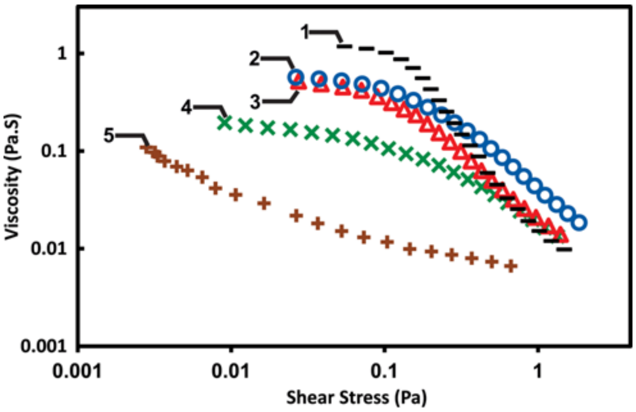

Fig. 3. Viscosity-shear stress behavior for SPA/Cr^{+3} systems prepared in distilled water after 7 days preparation at 40 °C with respective crosslinker/polymer ratio (w/w) of (1) 0, (2) 1/40, (3) 1/30, (4) 1/20 and (5) 1/10 (polymer concentration: 500 ppm).

Table 3. Herschel-Bulkley/power law coefficients of SPA solution and SPA/Cr^{+3} CDGs at different crosslinker/polymer ratio (w/w)

	Hershel Bakely coefficients			
Crosslinker/polymer ratio (w/w)	τ_0	μ_0	n	R^2
0	0.0128	0.2109	0.4138	0.9958
1/40	0	0.2377	0.4472	0.9983
1/30	0	0.1795	0.4438	0.9989
1/20	0	0.1245	0.5196	0.9981
1/10	0	0.0170	0.7984	0.9994

The rheological behavior of CDG solutions is systematically studied using the generalized Herschel-Bulkley equation (Eq. (1)).

$$\tau=\tau_0+\mu_0\gamma^n \tag{1}$$

It is used to model yield stress for different Cr^{3+} concentrations. The viscosity-shear rate curves are fitted to this equation by regression and the values of the constants obtained are given in Table 3. According to the regression data in Table 3, SPA solution has a yield stress, while CDGs solutions do not. That means their rheological behavior follows the power law equation (Eq. (2)).

$$\tau=\mu_0\gamma^n \tag{2}$$

The size of CDG particles affects their viscosity and other properties. For this reason, the size of CDG is measured with dynamic light scattering (DLS). DLS is a rapid, absolute, and nondestructive method for particle size measurements. The hydrodynamic radius (R_h) of CDG, obtained from DLS, is an important physical parameter, because a considerable amount of information about the size of molecules and the state of interaction between molecules and crosslinker (intra- or inter- crosslinking) can be obtained from the DLS analysis.

The size distribution for CDGs with various crosslinker/polymer ratios is shown in Fig. 4. The results indicate that CDGs with higher crosslinker content exhibit lower R_h values. Since the size of CDG is proportional to the number of intra-crosslink points of the gelling systems, it can be surmised that decreasing of CDG size by increasing of crosslinker concentration is due to increasing of the number of intra-crosslink point between anionic groups of polymer with Cr^{3+}.

For further investigation of the size and status of CDG particles, SEM images were prepared. Fig. 5 shows the SEM micrographs of the CDG systems. The sizes of CDG particles are decreased with increasing of crosslinker concentration. The size of the CDG particles with the respective crosslinker/polymer ratio of 1/10, 1/20,

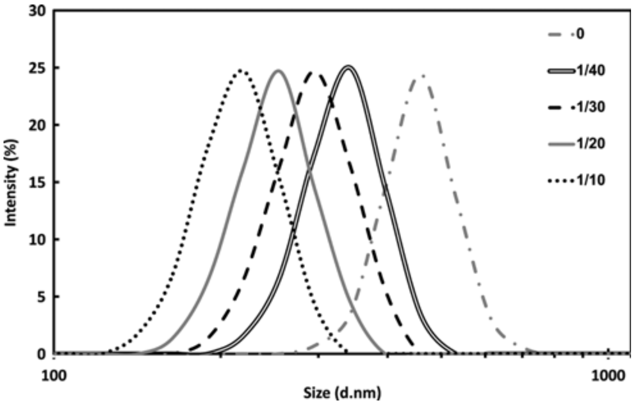

Fig. 4. Size distribution of SPA/Cr^{+3} systems at different crosslinker/ polymer ratio (w/w) (polymer concentration: 500 ppm).

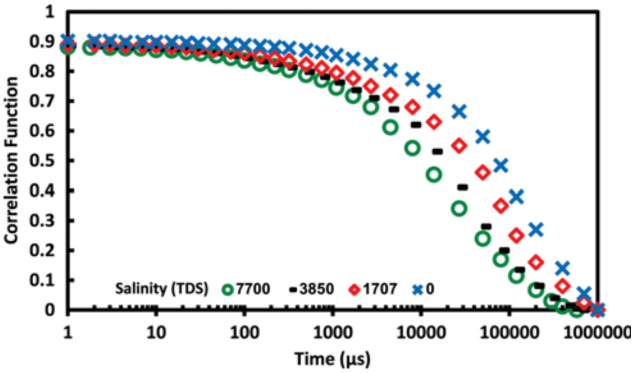

Fig. 6. Effect of salinity on correlation function of CDG (crosslinker/ polymer ratio (w/w): 1/20, polymer concentration: 500 ppm).

Table 4. Effect of temperature on viscosity of SPA/Cr^{+3} systems prepared in distilled water as a function of crosslinker/polymer ratio (Shear rate: 1 s^{-1}, polymer concentration: 500 ppm, after 7 days of preparation at the gelation temp.)

Gelation temperature (°C)	Crosslinker/ polymer ratio (w/w)	Viscosity (Pa·s)
40	0	0.253
40	1/20	0.106
40	1/10	0.0357
60	0	0.165
60	1/20	0.36
60	1/10	0.52
80	0	0.169
80	1/20	0.451
80	1/10	0.692

Table 5. Effect of salinity on viscosity of SPA/Cr^{+3} systems as a function of crosslinker/polymer ratio (Shear rate: 1 s^{-1}, polymer concentration: 500 ppm, after 7 days preparation at 40 °C)

Water salinity (ppm)	Crosslinker/polymer ratio (w/w)	Viscosity (Pa·s)
0	0	0.253
0	1/20	0.106
0	1/10	0.0357
1707	0	0.207
1707	1/20	0.0174
1707	1/10	0.0065
3850	0	0.0116
3850	1/20	0.0085
3850	1/10	0.0042
7700	0	0.0033
7700	1/20	0.003
7700	1/10	0.0021

1/30 and 1/40 varies in the range 0.1-0.3, 0.2-0.4, 0.2-0.5 and 0.3-0.7 µm. These sizes are approximately in consistent with those obtained from the DLS analysis (Fig. 4).

3. The Effect of Gelation Temperature

One of the main parameters in the CDG formation is the gelation temperature. In this study, the effect of gelation temperature on formation of CDGs is investigated at different temperatures (40 °C, 60 °C and 80 °C).

In Table 4, at gelation temperatures of 60 °C and 80 °C, the addition of crosslinker results in increase of the gel viscosity. A possible explanation for this is a proportional increase in number of inter-molecular crosslink points at elevated gelation temperatures leading to the formation of bulk gels, i.e., inter-molecular crosslinking between the anionic group of SPA and the cationic crosslinkers due to either enhancement of the molecular mobility or expansion of polymer chains at higher temperatures is increased. In this case the probabilities of polymer molecules and crosslinkers colliding with each other increase [41].

4. The Effect of Salinity

To evaluate the effect of salinity on CDG formation, CDG solutions were prepared in different salinities. The effect of salinity on viscosity in presence of different crosslinker concentration is displayed in Table 5. For all crosslinker concentrations, increasing of salinity decreases the viscosity of the CDG systems, which was said to be due to the formation of polymer coils by intra-molecular crosslinking. Since salt will promote the collapse of polymer coils [1], the decrease in viscosity is expected to be higher in high salinity systems. The trend of decreasing viscosity in presence of salt agrees well with the observations made by Bjorsvik et al. [35] and Mack et al. [30].

The effect of salinity on size of CDGs particles was investigated by correlation function of DLS measurement. It is identified that the correlation function is related to the particle size. The speed of particles that are being moved by Brownian motion is related to the size of the particles (Stokes-Einstein equation). In correlation function-time curve, the time when decay starts indicates the mean size of particle. If the size of particles becomes small, the decay in this curve begins at earlier times [42].

The change of correlation function with time for each sample at different salinities after seven days gelation time at 40 °C is shown in Fig. 6. The size of CDGs decreases with increasing salinity of CDG solutions. The cations in the solution screen the electrostatic (repulsive) interactions between the negative (carboxylate and sul-

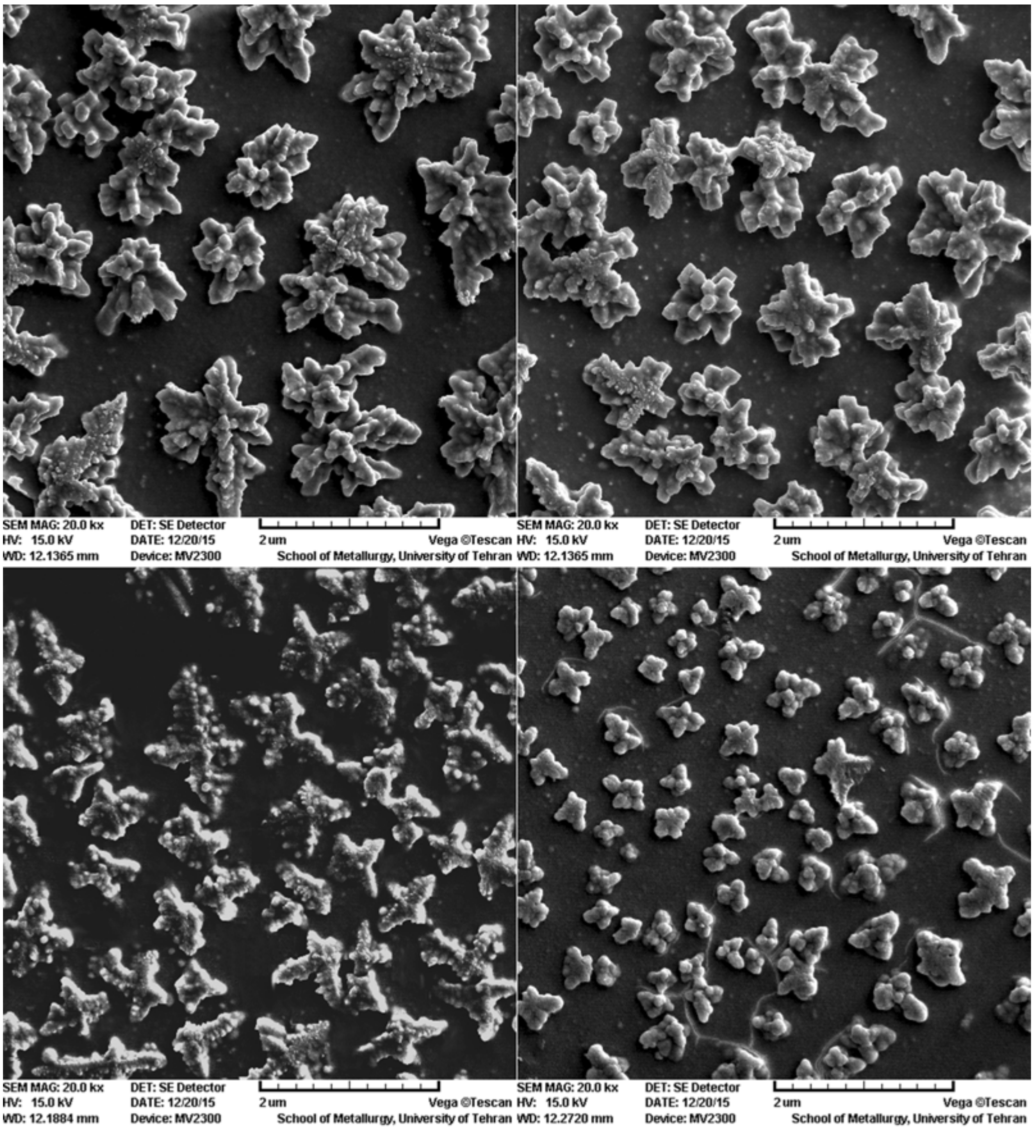

Fig. 6. Comparison of SEM photographs for SPA/Cr^{+3} systems prepared in distilled water after 7 days keeping at 40 °C gelation temperature with respective crosslinker/polymer ratio (w/w) of (a) 1/40, (b) 1/30, (c) 1/20 and (d) 1/10 (polymer concentration: 500 ppm).

fonate) charges carried by the polymer, leading to chain shrinking and reduction of CDGs sizes.

5. The Effect of Polymer Concentration

Fig. 7 shows the effects of polymer concentration on steady shear viscosity for samples containing different crosslinker/polymer concentrations. As will be seen for polymeric crosslinked solutions, the value of viscosity may be regarded as a measure of intermolecular to intramolecular bonds ratio. It has been reported that when the polymer concentration is above a critical level, known as the overlap concentration, intermolecular crosslinking between two or more polymers will occur, and continued intermolecular crosslinking will inevitably lead to the formation of a highly viscous gel [35,43]. Therefore, the viscosity is expected to increase with the crosslinker concentration. This is exactly what happened to the systems with 2,000 ppm polymer content. On the other hand, as can be seen in Fig. 2 the viscosity reduces with the crosslinker concentration, which was attributed to the increased number of

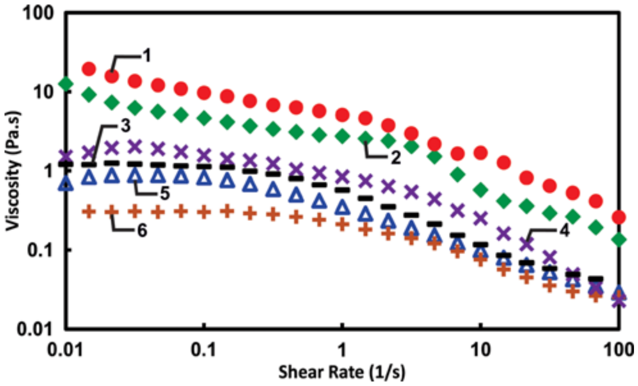

Fig. 7. Viscosity-shear rate behavior for SPA/Cr^{+3} systems prepared in distilled water after 7 days at 40 °C with respective polymer concentration-crosslinker/polymer ratio (w/w) of (1) 2000-1/10, (2) 2000-1/20, (3) 2000-0, (4) 1000-1/10, (5) 1000-0 and (6) 1000-1/20.

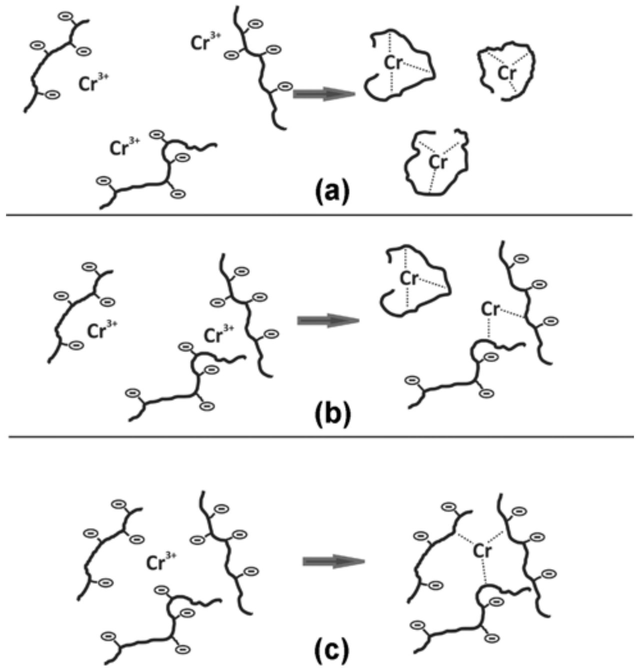

Fig. 8. Schematic of CDG formation (a), gelation at critical overlap concentration (b) and bulk gel formation (c).

intramolecular crosslinks. However, for the systems with 1,000 ppm polymer content, the viscosity shows no meaningful trend. This behavior is thought to be due to the competition between intra- and inter-crosslink interactions. Therefore, it is believed that this level of concentration is the critical overlap polymer concentration above which the bulk gelation process starts [43]. Whether the solution is dominated by intra- or intermolecular interactions depends on a number of factors, including polymer type, molecular weight, polymer concentration, ratio of polymer to crosslinker, salinity, reaction time and temperature [23].

Fig. 8 schematically illustrates that in the dilute regime the average distance between distinct polymer molecules is much larger than the coil size, and intermolecular interactions are negligible. According to the Cage effect and Flory-Huggins theories, when the polymer concentration is low, the possibility of the presence of more than one polymer in the cage of the crosslinker is infrequent, and consequently intra-crosslinking reaction will be performed [32]. However, as the concentration increases intermolecular interactions become significant and bulk gel forms.

6. Aging Effect

The thermal, mechanical and chemical degradation of the polymeric systems are of the major problems in polymer flooding. In this study the effects of high temperature and high salinity on the stability of polymeric systems were investigated. Therefore, the shear viscosity of SPA polymer solution and CDGs before and after thermal aging at 90 °C in the absence (Fig. 9) and presence (Fig. 10) of salinity were studied. Fig. 9 indicates that in the absence of salinity the shear viscosity of SPA solution decreases more than that of CDG as a result of thermal aging. For polymers thermal and thermo-oxidative degradations occur at elevated temperatures. These degradations start when a bond breaks and molecular weight decreases [44]. Fig. 9 shows that due to formation of intramolecular crosslinking, CDG shows a higher resistance to bond breakage and is more thermally stable than SPA polymer [23]. In addition, crosslinks bonds present in polyacrylamide/Cr^{3+} gels are kinetically reactive toward ligand exchange, and acetate is a thermodynamically weaker ligand for Cr^{3+} than is polyacrylamide. Therefore, at high temperature a new structure forms with the bonding between Cr^{+3} and polyacrylamide and the gel is stabilized [45].

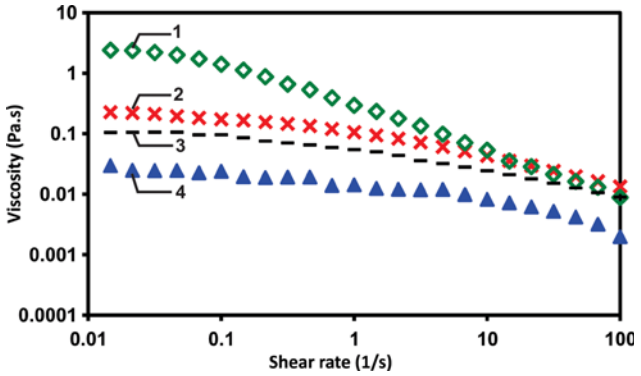

Fig. 9. Effect of thermal aging in distilled water on shear viscosity of (1) SPA solution before aging, (2) CDG with crosslinker/polymer ratio (w/w) of 1/10 before aging, (3) CDG with crosslinker/polymer ratio (w/w) of 1/10 after aging, (4) SPA solution after aging (polymer concentration: 500 ppm, aging temp.: 90 °C, aging time 30 days).

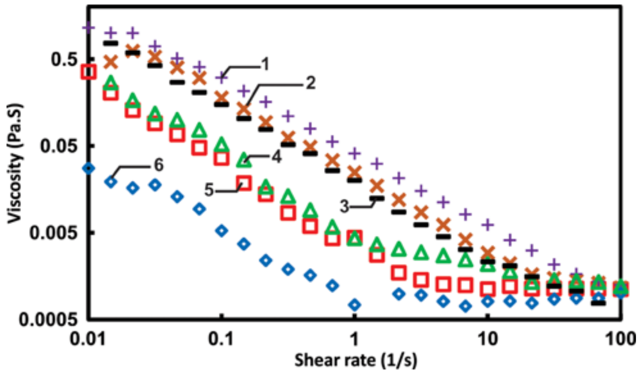

Fig. 10. Effect of thermal aging in electrolyte media on shear viscosity of SPA solution and its CDG samples with respective crosslinker/polymer ratio (w/w) of (1) 0 before aging, (2) 1/20 before aging, (3) 1/10 before aging, (4) 1/20 after aging, (5) 1/10 after aging and (6) 0 after aging (polymer concentration: 500 ppm, aging temp.: 90 °C, TDS: 7,700 ppm, aging time 30 days).

The viscosity of the polymeric systems decreases in mixing with reservoir water. In this regard, the effect of the salinity after mixing with saline water on the stability of polymer systems is investigated. Note that despite the systems prepared originally in saline solution for evaluation of the effect of salinity on their formation and initial rheological properties (section 3.4), all of the polymeric systems here were prepared in distilled water out of which some were then subjected to salinity. The prepared polymeric systems were mixed with saline water for 1 day at 40 °C and the viscosity

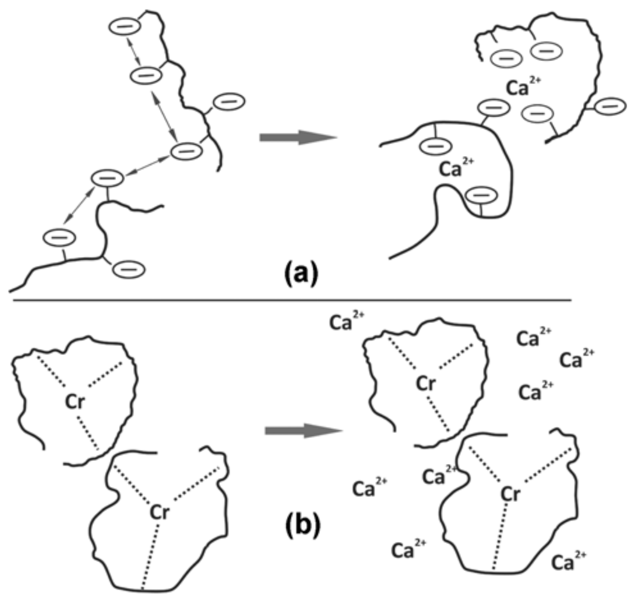

Fig. 11. Schematic of interaction of divalent cations with SPA polymer (a) and CDG (b).

was measured. Then they were subjected to a thermo-chemical aging cycle of 30 days at 90 °C. Fig. 10 shows the synergistic effect of thermal and chemical aging processes. As can be seen, the shear viscosity for SPA solution is decreased in electrolyte media more than that of CDGs due to the thermo-chemical aging. The aging in presence of salinity is more pronounced than that in its absence. Therefore, other than the above mentioned justifications for the thermal aging, the following explanation may be added for the case that salts are present.

Fig. 11 shows the mechanism of the chemical interaction between divalent cations (Ca^{2+}) with CDG and SPA polymer. In the presence of the monovalent and divalent cations (Na^+ and Ca^{2+}) in brines solution, negative charges along the carboxylate and sulfonated groups (SO_3^-) of SPA polymer chain are screened from each other by association with cations from the solution. Apparently, the more collapsed state of the molecule in salt solution inhibits the formation of entanglements and other inter-molecular interactions. On the other hand, due to the higher degree of intra-molecular crosslinking in CDGs, less charge screening occurs due to divalent cations.

The literature shows that the viscosity of polyacrylamide, however, is substantially affected by divalent ions, and it is generally approved that strong interaction between divalent ions and the carboxylate groups of polyacrylamide is the main precipitation mechanism in high salinity [46-49]. The white precipitate observed in Fig. 12(a) confirms this phenomenon. Fig. 12(b) shows that after 30 days of thermo-chemical aging, CDG solution is clear with no sign of precipitation, indicating the exceptional thermochemical stability of these systems.

CONCLUSIONS

Colloidal dispersion gel systems based on sulfonated polyacrylamide (SPA)/chromium triacetate (Cr^{3+}) were prepared. The effects of crosslinker, polymer concentration, salinity, and gelation time and temperature on the formation and rheological behavior of CDGs were studied. The effects of crosslinker concentration, formation time and salinity on CDG size and size distribution were surveyed by dynamic light scattering. The thermal and thermochemical stability of these systems were investigated at 90 °C for 30 days. Based on this study, the following conclusions can be drawn:

1- For SPA/Cr^{3+} systems containing 500 ppm SPA, at gelation temperature of 40 °C viscosity decreased by increasing of crosslinker concentration, which indicates colloidal dispersion gels formation, while at gelation temperatures of 60 °C and 80 °C, viscosity increased by increasing of crosslinker concentration, which may be attributed to bulk gel propagation.

2- According to steady shear and DLS results, the shear viscosity and size of CDGs particles decreased with increasing of preparation time.

3- Investigation of the size and status of CDG particles by DLS method and SEM images showed that size of CDGs particles decreased with increasing of the Cr^{3+} concentration.

4- SPA solution has yield stress, while CDG systems do not.

5- Salinity did not disturb the formation of CDGs. However, the size and viscosities of CDGs decreased with increasing salinity.

6- For SPA/Cr^{3+} systems containing 2,000 ppm SPA at gelation temperature of 40 °C, viscosity increased with increasing crosslinker concentration, which showed that bulk gels were formed. Further investigations showed that 1,000 ppm SPA can be introduced as threshold concentration from CDG to bulk gel formation at this gelation temperature.

7- After 30 days of thermo-chemical aging, CDG solution had a minimal viscosity loss, which is in agreement with its appearance being clear with no sign of precipitations, indicating the exceptional thermo-chemical stability of these systems.

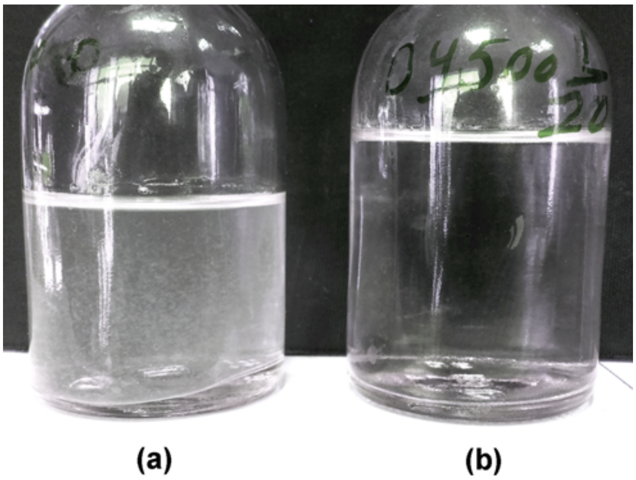

Fig. 12. SPA solution (a) and its CDG sample with crosslinker/polymer ratio (w/w) of 1/20 (b) after 30 days thermal aging in electrolyte media.

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