

EFFECTS OF NANOPARTICLES AND SURFACTANT CHARGE GROUPS ON THE PROPERTIES OF VES GEL

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Abstract - Application of viscoelastic surfactant (VES) fluids in hydraulic fracturing is still in the development stage, though shear thinning behavior and water solubility are the two important characteristics behind increasing interest in their use in fracturing jobs. Effects of ionic characteristics and the concentration of different surfactants on the rheological properties of VES fluid have been investigated in detail in the present study for a number of surfactant systems. Phase behavior of the system was studied and the gel region was identified. Effects of alkali on the viscosity, thermal stability, and miscibility (in water) of the developed gel were also investigated. Dynamic rheological study was carried out to determine the storage modulus and loss modulus. This study shows that mixed anionic-anionic system gives improved rheology compared to single anionic and mixed anionic-zwitterionic surfactant systems.

Keywords: Hydraulic Fracturing; Viscoelastic gel; Surfactant based fluids; Rheology; Nanoparticles.

INTRODUCTION

Use of surfactants in various applications is almost as old as human civilization. They find wide application in industry because of their remarkable ability to influence the properties of surfaces and interfaces. Surfactants are applied at all stages in the petroleum recovery and processing units, starting from well drilling, hydraulic fracturing, EOR to other production operations. Surfactants generally form aggregates, i.e., micelles, where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding liquid when dissolved in an aqueous phase. Aggregates may be formed in different shapes: spherical or cylindrical micelles or lipid bilayers. The shape of the aggregates depends on the chemical structure of the surfactants, namely the balance in size between hydrophilic head and hydrophobic tail. Thus, variation

in the head and tail groups will change the entire characteristics of the material formed with surfactants and other chemicals.

Use of viscoelastic surfactant based gels in fracturing fluids creates ordered structures, resulting in increased viscosity and elasticity without leaving any post fracture residue in the formation (Jennings, 1996; Armstrong *et al.*, 1996). Fracturing fluid is injected at a rate and pressure greater than parting pressure of the rock to create the fractures (Samuel *et al.*, 1997). To prevent the fracture face from closure because of flow back of fracturing fluid, proppants are incorporated in the fluids, which are left behind after the job, allowing conductive channels to remain open. Therefore, viscosity of the fluids is an important factor as it transports the proppant material into the fractures. "Premature Screenout", i.e., proppant drop out in the wellbore or fracture can happen because of low viscosity of the fracturing fluid (Kesavan and

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Homme, 2007). Use of Viscoelastic Surfactant based gels in fracturing fluids is a relatively new phenomenon, which uses surfactants in combination with inorganic salts or other surfactants to create ordered structures, resulting in increased viscosity and elasticity (Jennings, 1996; Armstrong *et al.*, 1996). Viscoelastic surfactants are very small molecules with a molecular size 5,000 times smaller than guar molecules. They consist of a hydrophilic head group and a long hydrophobic tail (Yuan *et al.*, 2012). They form elongated micellar aggregates in the presence of brine. Above a certain critical surfactant concentration, the micellar structures entangle and form a mesh-like structures. Depending on the size and shapes of the surfactants, ionic charges and the counter ions, ordered structures start to form, which increases viscosity and elasticity. The reverse mechanism is true for breaking these systems. The structures can be disrupted by adding an other surfactant, ionic additives and hydrocarbons from the formation, mutual solvents or other solvents or can be diluted by additional formation water as the surfactant concentration eventually falls to a level at which insufficient numbers of micelles are present to entangle and viscosity is lost (Dantas *et al.*, 2006).

When micelles are disassociated by shear energy, the rheological behavior of VES fluids is similar to water, or nearly Newtonian; yet viscosity and elastic behavior recover when the disrupting energy is removed. VES requires less energy to pump than that required by conventional polymer fluids, effectively reducing wellsite pump-horsepower requirements (Nasr-El-Din *et al.*, 2003; Khair *et al.*, 2011).

Viscoelastic surfactant based gels can be obtained from microemulsified systems composed of aqueous phase, oil phase, surfactant and cosurfactant which are thermodynamically stable, iso-tropic and macroscopically homogenous dispersions of two immiscible fluids stabilized with either surfactant molecules alone or mixed with a cosurfactant (Yuan *et al.*, 2012). Winsor's classification is used to study the phase diagram (Dantas *et al.*, 2003a; Dantas *et al.*, 2003b). The phase regions were obtained as Winsor I (O/W): A microemulsion phase in equilibrium with an excess organic phase, Winsor II (W/O): A microemulsion phase in equilibrium with an excess aqueous phase, Winsor III (bicontinuous or middle phase microemulsion): A three phase system where the microemulsion is in equilibrium with both excess organic and aqueous phases, and Winsor IV (homogeneous): a macroscopically homogenous system only consisting of a microemulsion phase (Dantas *et al.*, 2003; Dantas *et al.*, 2006; Mehta and Kaur, 2011;

Thampi *et al.*, 2014). High viscoelastic properties with wormlike micellar growth have been reported in anionic and mixed-surfactant systems consisting of anionic-anionic, cationic-anionic and ionic-zwitterionic surfactants (Angelescu *et al.*, 2003; Koehler *et al.*, 2000; Tanford, 1972).

In some of our previous studies on designing of new surfactant-based hydraulic fracturing fluid, a microemulsion gel domain region was identified for an anionic surfactant (SDS) and isoamyl alcohol as cosurfactant at a cosurfactant-to-surfactant (C/S) ratio of 0.5 (Bajpai *et al.*, 2010), and for sodium oleate as surfactant and two branched alcohols, 2-methyl butan-2-ol, 3-methyl butan-1-ol as cosurfactant (Thampi *et al.*, 2014). The results of the rheological, proppant suspension and thermal study of the gel were found to be suitable for CBM, clay rock stimulation.

Also, in our previous study, a comparative rheological study on the VES-based gels prepared from single surfactant (anionic, SDS) and mixed-surfactant (zwitterionic, CAPB, and anionic, SDS) systems was performed to evaluate the performances of the different surfactant system gels (Baruah *et al.*, 2014). In the present study, we report a rheological study on the mixed VES-based gels prepared from two anionic mixed surfactants (SDS and ALS) as a function of surfactant type, surfactant concentration, temperature, alkali concentration, and addition of nanoparticles and we have compared this with single surfactant SDS studies and anionic and zwitterionic SDS+CAPB by reference to our previous studies (Baruah *et al.*, 2014).

MATERIALS AND METHODS

Materials

Sodium lauryl sulfate, with the common name sodium dodecyl sulfate (SDS), $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}]$, an anionic surfactant, was procured from LobaChemie Pvt. Ltd., Mumbai, India. Liquid anionic surfactant ammonium lauryl sulfate, with the common name ammonium dodecyl sulfate (ALS), $[\text{C}_{12}\text{H}_{29}\text{NO}_4\text{S}]$, was obtained from Alpha Chemicals Pvt. Ltd., Navi Mumbai, India. Isoamyl alcohol (3-methylbutan-1-ol), used as cosurfactant, was purchased from Merck Specialties Pvt. Ltd., Mumbai, India. Pine oil was used as the organic phase. Samples were prepared using distilled water. Sodium hydroxide (NaOH) of purity greater than 98% was obtained from LobaChemie Pvt. Ltd., Mumbai, India. Silicon di-

oxide (SiO_2) nanoparticles with an average particles size of 15 nm and purity of 99.5% were obtained from SRL Pvt. Ltd., Mumbai, India. All chemicals used were of high purity and hence used as received.

Methods

Preparation of the Pseudo-Ternary Phase Diagram

Determination of the gel region in the phase diagram is important to identify the appropriate composition for the gel with the most suitable properties. The pseudo-ternary phase diagram was constructed using a water titration method at fixed temperature ($25 \pm 1^\circ\text{C}$). For easy representation, the two constituents, namely, surfactant and cosurfactant are kept in a fixed proportion, forming a “pseudoconstituent”. The phase diagram was plotted with a cosurfactant to surfactant (C/S) ratio of 1:2 by weight. This ratio can be varied for further studies. For the mixed surfactant system, the ratio of ALS to SLS was fixed at 1:2 by weight. The ratio of oil to the mixture of surfactant and cosurfactant was varied from 1:9 to 9:1 by weight. The preparation of the phase diagram and surfactant based gel were described in Baruah *et al.*, 2014.

Rheological Measurements

Viscosities of gels were measured at variable shear rate and temperature. A Parr Physica US 200 rheometer (Anton Parr, Graz, Austria) with cone-and-plate geometry (50 mm cone diameter and a cone angle of 2°) maintained at a distance of 500 μm was used for measuring the viscosities of samples. The test temperature was varied from 30 to 80°C for VES samples. At constant set temperature, the shear rate was varied from 1 to 1000s^{-1} for all the tests. A modular compact rheometer, MCR-302 (Anton Paar, Austria), was used for frequency sweep measurements and again cone-and-plate geometry maintained at a gap size of 500 μm was used for testing VES samples. The cone (CP 50-1/Q1) had a diameter of 50 mm and a cone angle of 1° .

Miscibility Tests

To get an estimation of breaking characteristics of the prepared VES gel samples, miscibility tests were performed. Kinematic viscosity of the solution was determined using a Cannon Fenske viscometer with different orifice diameters as required (25, 50, 150, 200, and 300 mm). The test was carried out in presence of distilled water by mixing the gel with water

at different proportions. The reduction in viscosity was reported as kinematic viscosity (centistokes, cSt), then converted to absolute viscosities (centipoises, cP). The gel-to-water ratio was fixed at 1:3, 1:2, 1:1, 2:1, and 3:1. The test temperatures were varied from 30 to 60°C .

RESULTS AND DISCUSSION

Phase Studies of Quaternary Systems with (ALS + SDS) as Mixed Surfactant System

The phase diagram of the quaternary system, with distilled water as the aqueous phase, iso-amyl alcohol as the co-surfactant and pine oil as the organic phase with the mixed surfactant system (ALS+SLS), is shown in Figure 1, at a cosurfactant to surfactant (C/S) ratio of 0.50. A solid-liquid biphasic (SL) region exists, along with a semi-transparent solution at higher concentration of surfactant. A three-phase (3E) region exists near a water-rich region at lower surfactant concentration. In the 3E region, a milky emulsion phase lies in between a thin oil layer (above) and water phase (bottom). Also a milky emulsion with excess water, i.e., a two-phase (2E) region, exists. A milky liquid - single emulsion (1E) phase exists near the oil-rich corner. A microemulsion phase (WIV) exists, which is a transparent single isotropic liquid. The range of formation of a microemulsion zone depends on the physicochemical properties of the oil, aqueous phases, surfactant type, presence of a very low surface tension at the oil-water interface and high fluid interfacial film of surfactant and last, association and penetration of oil molecules in the interfacial surfactant film (Rajib and Bidyut, 2005; Hou, 1987). This area corresponds to an area of mutual solubility in both the systems consisting of mixed-surfactant/co-surfactant/pine oil/water and it occurs in the water-rich domain. A clear and viscous microemulsion (GEL) region exists near this region. Also a viscous, white fluid (WV) region exists near this GEL region. This clear and viscous gel region is our area of interest for the preparation of viscoelastic surfactant based fracturing fluid.

For the accomplishment of the rheological study, two points were chosen in the gel region:

Point 1: 21.33 wt % surfactant, where ALS is 7.11 and SLS is 14.22, 10.6 wt % cosurfactant, 22.66 wt % oil, and 51 wt % water, i.e., 32% C/S at a constant water to oil ratio of 3:1.

Point 2: 22.66 wt % surfactant, where ALS is 7.55 and SLS is 15.10, 11.33 wt % cosurfactant,

22.66 wt % oil, and 51 wt % water, i.e., 34% C/S at a constant water to oil ratio of 3:1.

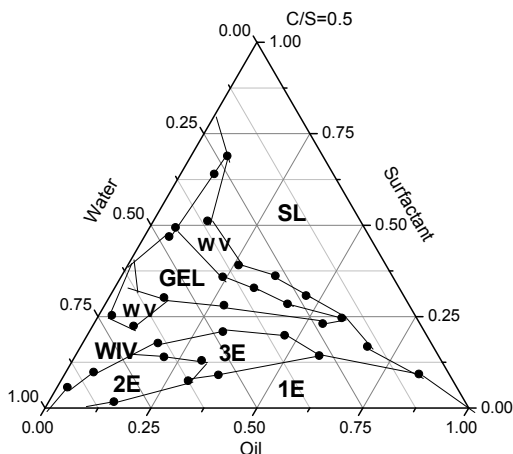


Figure 1: Pseudo-ternary phase diagram for Sodium Lauryl Sulfate+ Ammonium Lauryl Sulfate/isoamyl alcohol/pine oil/water system.

Steady Shear Rheology of VES Gels

Figures 2-5 present the values of viscosity for different surfactant (ALS+SLS) based viscoelastic gels at 32 and 34% C/S concentration with 0.05% NaOH and 0.1% NaOH. Figures 2 and 3 present the effect of addition of NaOH on 34% C/S ALS+SLS at 30 and 80 °C respectively. For the shear rate range between 1 to 1000 s^{-1} , 34% C/S ALS+SLS with 0.1% NaOH always presented higher value of viscosity than 34% C/S ALS+SLS at 0.05 and 0% NaOH. Raising the pH of VES fluids by addition of alkali, i.e., sodium hydroxide (Figure 2) results in viscosity enhancement for any test temperature between 30 to 70 °C. This is due to the fact that addition of NaOH (counter ions) to the solution decreases the electrostatic repulsive forces between surfactant molecules in a micelle and also decreases the spontaneous curvature of the aggregates, thus promoting micelle growth (Hoffmann *et al.*, 1982; Pal 1998; Acharya, 2007). As a result, long, flexible anionic wormlike micelles with higher relaxation time and zero shear viscosity are formed in the solution, which resembles a polymer solution of high viscoelasticity (Thampi *et al.*, 2014; Baruah *et al.*, 2014).

Figure 4 presents the variation of viscosity with shear rate (1-1000 s^{-1}) for 34% C/S (ALS+SLS) with 0.1% NaOH within the shear rate range of 1 to 1000 s^{-1} at temperatures of 30, 60, 70 and 80 °C. From the figure it is clear that the viscosity decreases with increase in temperature and shear rate up to 60 °C and beyond this temperature the viscosity increases. The former behavior is due to the fact that the aggre-

gates formed move away from each other and a continuous decrease in viscosity is observed. At the temperatures beyond 60 °C, viscosity increases because of increased surfactant-water interactions, and hence, more surfactant penetrates into the aqueous phase, increasing the micelle volume and resulting in increased viscosity (Dantas *et al.*, 2003; Yang *et al.*, 2015). But at increased temperature above 70 °C (Figure 3), addition of alkali forbids this enhanced surfactant-water interaction effect because addition of counter ions resulted in decreased electrostatic repulsion between surfactant molecules. Therefore, at 80 °C temperature, 34% ALS+SLS with 0% NaOH presented a higher value of viscosity than the VES fluids in the presence of alkali.

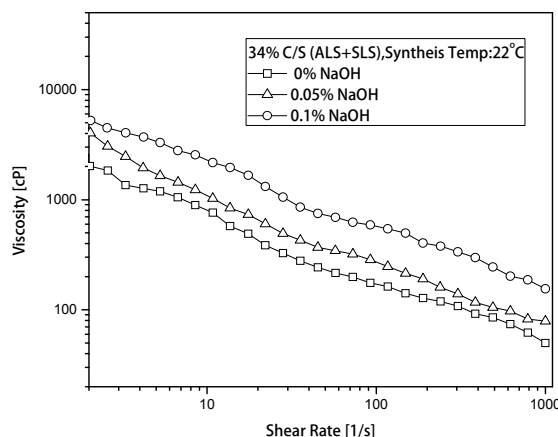


Figure 2: Effect of alkali (NaOH) on SBG: 34%C/S (ALS+ SLS) at 30 °C.

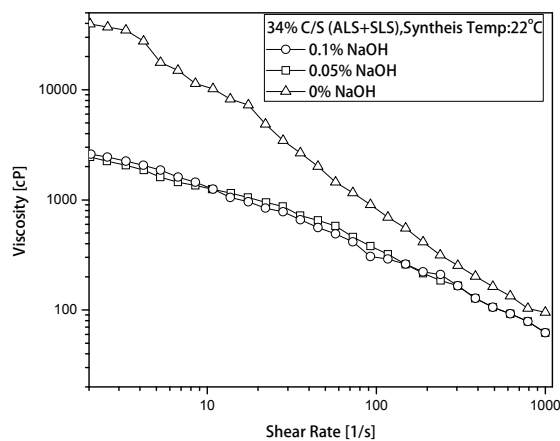


Figure 3: Effect of alkali (NaOH) on SBG 34%C/S (ALS+ SLS) at 80 °C.

Figure 5 shows the variation of viscosity for 32% and 34% ALS+ SLS with concentration of NaOH varying from 0 to 0.1% NaOH. 34% C/S always presented a higher viscosity value at any test temperature between 30-60 °C and any shear rate than

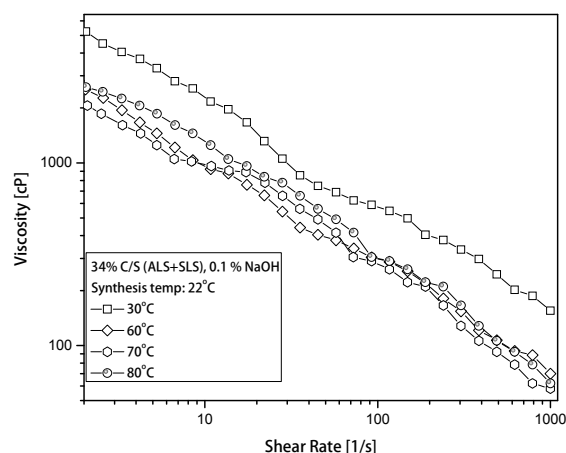


Figure 4: Variation of SBG i.e. 34% C/S ALS+SLS with Shear Rate at different temperature for 0.1% NaOH concentration.

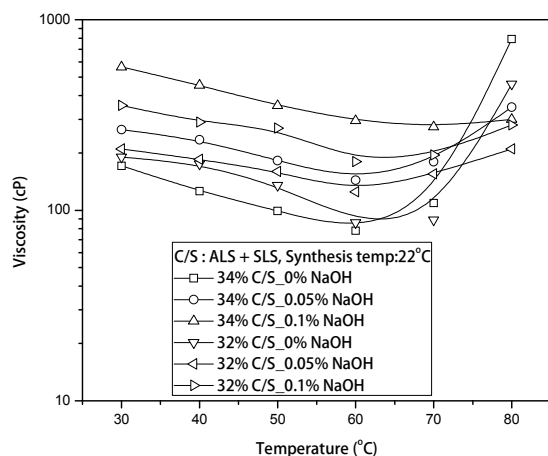


Figure 5: Comparison of SBG of 32% and 34% C/S ALS+SLS at 100 s^{-1} Shear Rate for 0%, 0.05% and 0.1% NaOH concentrations.

32% C/S. This is because increased surfactant concentration enhances the growth and entanglement of worm-like micelles, i.e., Micellar Aggregation Number (N) increases at higher surfactant concentration and N decreases with increase in temperature (Pal, 1998). It can be observed from Figures 2 to 5 that the apparent viscosity decreases with increasing shear rate for all temperatures, indicating the shear thinning nature of the fluids. The reduction in viscosity is due to breaking of a network of wormlike micelles as the micelles align themselves in the direction of shear, which occurs even in the presence of alkali at increased temperature. Yet viscosity and elastic behavior are recovered once the disrupting energy is removed. In particular, the molecular thermodynamic theory describes this ionic/ionic interaction and mi-

cellar growth as it occurs due to the modification of the apparent surface per headgroup and screening of the electrostatic repulsion between the headgroups. The proper balance between the different contributions to the free energy of micellization can result in maximization of the aggregation number for particular compositions (Pal, 1998; Grillo, 2014).

The mixed surfactant system was selected so as to see the result of interaction of two anionic surfactant systems and their effect on the rheology as compared to single (anionic, SLS) and mixed (anionic, SLS and zwitterionic, CAPB) surfactant systems, which were studied earlier (Baruah *et al.*, 2014). Though gel was formed in increased surfactant concentration of 32% for 3:1 water oil ratio in case of mixed anionic-anionic surfactant system but thermal stability was found to be increased by 10°C from the single surfactant system. Table 1 presents viscosity values at 100 s^{-1} shear rate for 32% C/S SLS, 30% C/S(SLS+CAPB) and for 32% C/S (ALS+SLS). Several laboratory studies and field experiences with polymeric fluids led to the development of an important guideline that the fluid should have a viscosity of 100 cP at 100 s^{-1} for adequate proppant transport as this shear rate value also represents the field condition of pumping the fracturing fluid down the wellbore (Zana and Kaler, 2007). This leads to the selection of a constant shear rate value of 100 s^{-1} . Viscosity of 32% C/S (ALS+SLS) is greater than single SLS surfactant system (32% C/S SLS) but lower than mixed anionic-zwitterionic 30% C/S(SLS+CAPB) surfactant system. Though viscosity is lower than the anionic-zwitterionic surfactant system, but the present anionic-anionic system is more cost effective and readily available surfactants in the markets than zwitterionic surfactants. Viscosity is increased due to increase in charge density. The anionic-anionic mixed surfactant system is more surface active than single SLS or ALS systems. The two surfactant systems have a different rheological behavior, even though they are very similar in their chemical composition. The differences here are due to the distribution of charge on the cylindrical micelles (Hoffman, 1994). Also, the viscosity of this anionic-anionic mixed surfactant system is less than that of the anionic-zwitterionic mixed surfactant system, as the effect of electrostatic attraction of the hydrophilic part between the cationic portion of the zwitterionic and the anionic portion of the dodecyl sulfate ion is higher than the charge density effect of the anionic-anionic mixed surfactant system.

Table 1: Viscosity (cP) values at 100 s⁻¹ shear rate for 32% C/S SLS, 30% C/S (SLS+CAPB) and for 32% C/S (ALS+SLS) with reference from Baruah *et al.* (2014).

Temp, °C	32%C/S SLS		30%C/S(CAPB+SLS)		32%C/S(ALS+SLS)	
	0% NaOH	0.1% NaOH	0% NaOH	0.1% NaOH	0% NaOH	0.1% NaOH
30	142	290	240	360	190	355
40	60	240	190	310	170	290
50	48	190	140	275	110	270
60	35	160	110	220	90	180

Effect of addition of Nanoparticles

In VES fluids, nanotechnology application is used for maintaining viscosity at high temperatures and controlling fluid loss without damaging the formation. For this study, 500 ppm inorganic silicon dioxide (SiO₂) nanoparticles were selected, which displayed unique surface morphology and reactivity. Viscosity is the measure of a fluid's resistance to gradual deformation by tensile or shear stress. More resistance to viscosity loss with an increase in temperature is a qualitative analysis of thermal stability which had been used as a parameter for thermal stability by many authors like Crews and Huang (2008), Tamas *et al.* (2014), Baruah *et al.* (2014) etc. 34% C/S (ALS+SLS) with 0.1% NaOH and 500 ppm SiO₂ nanoparticles exhibited higher resistance to high temperatures and shear rate by maintaining a higher value of viscosity; thus, they can be considered to be more thermally stable than 34% C/S (ALS+SLS) + 0.1% NaOH without nanoparticles. These nanometer-scale particles react with VES micelles by chemisorptions and surface charge attraction to stabilize fluid viscosity at high temperatures and produce a pseudofilter cake of viscous VES fluid that significantly reduces the fluid loss rate. In other words, a high density 3D-network of worm-like micelles is obtained, which makes the micelles more thermally resistant to higher temperature (Crews and Huang, 2008). The increase in thermal stability by addition of SiO₂ nanoparticles can be observed in Figure 6. When nanoparticles are added to the VES solution, they will associate or create intramicellar "pseudo-crosslinking", giving a much stronger dynamic micelle network (Huang and Crews, 2008). Also, addition of nanoparticles leads to the formation of micelle-particle junctions that effectively join two or more micelles (Crews and Huang, 2008).

The temperature increase leads to microdrop mobility intensification, which influences the activation energy of the system. This viscosity-temperature relationship can be explained by Arrhenius type equations applied to the cumulative effect described by the shear stress (Tamas *et al.*, 2014).

$$\eta = A.e^{\frac{E_a}{RT}}$$

where E_a is the viscous flow activation energy (J mol⁻¹); R is the universal gas constant, having a value of 8.314 J.K⁻¹ mol⁻¹; T is the absolute temperature and A represents a material constant (Pa s) (Hassan *et al.*, 1998).

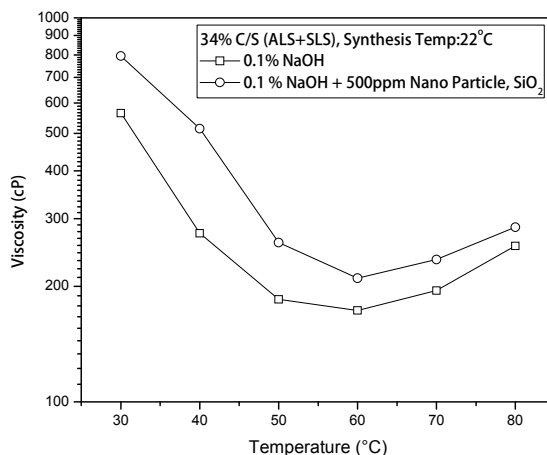
**Figure 6:** Effect of addition of 500 ppm SiO₂ nanoparticles to 34% C/S ALS+SLS with 0.1% NaOH for different temperatures at 100 s⁻¹ shear rate.

Figure 7 shows the plot of the logarithm of the viscosity versus the reciprocal of the temperature for 34% C/S ALS+SLS, 0.1% NaOH with 0 ppm and 500 ppm nanoparticles for test temperatures between 30-60 °C. A near linear plot was obtained for 34% C/S ALS+SLS, 0.1% NaOH + 500 ppm nanoparticles ($R^2 = 0.9605$ with standard error of 0.150), which is in good agreement with the Arrhenius type equation, while the plot for 34% C/S ALS+SLS, 0.1% NaOH shows some deviation from linearity ($R^2 = 0.8932$ with standard error of 0.217). However, it was used for the estimation of activation energy values, as no other established correlation is available in the literature. All of the relevant statistical information for constructing a linear regression equation is presented in Table 2.

Table 3 gives the ANOVA results for linear plots for both the gels. The significance value of 0.020 (<0.05) for 34% ALS+SLS+ 0.1% NaOH with 500 ppm SiO₂ nanoparticles supports the linear relationship between $\ln \eta$ and $(1/T)$, while the significance value of 0.055 (>0.05) for 34% ALS+SLS+ 0.1% NaOH means there is some deviation from a linear relationship.

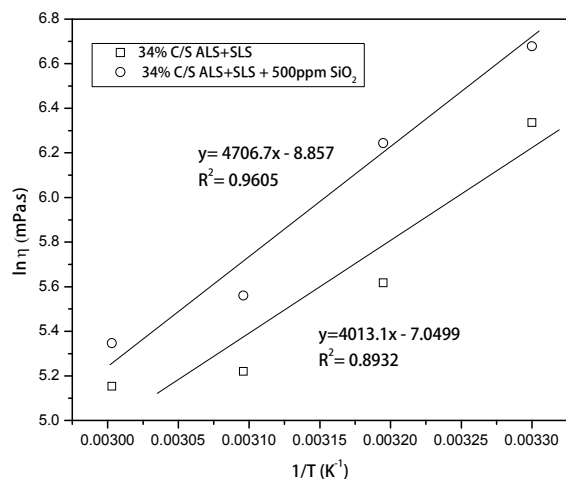


Figure 7: Plot of $\ln \eta$ vs $1/T$ for 34% C/S ALS+SLS and 34% C/S ALS+SLS + 500 ppm SiO₂ at 0.1% NaOH for 303-330K temperature range.

Table 2: Table for Coefficients of Arrhenius linear plot with their standard error and significance value for 34% C/S ALS+SLS+0.1% NaOH with 0 and 500 ppm SiO₂.

34% C/S ALS+SLS+0.1%NaOH	Unstandardized Coefficients		Significance
	B	Std. Error	
For 0 ppm SiO₂			
Slope	4013.143	981.004	0.055
Intercept	-7.050	3.090	0.150
For 500 ppm SiO₂			
Slope	4706.724	675.213	0.020
Intercept	-8.857	2.127	0.053

Table 3: ANOVA table for linear plots for 34% C/S ALS+SLS+0.1% NaOH with 0 and 500 ppm SiO₂.

34% C/S ALS+SLS+0.1% NaOH	Sum of Squares	Degree of Freedom	Mean Square	Significance
1. For 0 ppm SiO₂				
Regression	0.790	1	0.790	0.055
Residual	0.094	2	0.047	
Total	0.885	3		
2. For 500 ppm SiO₂				
Regression	1.087	1	1.087	0.020
Residual	0.045	2	0.022	
Total	1.132	3		

Values of the activation energy were calculated using the slope value $[E_a/RT]$ of the linear plot, as

shown in Figure 7 and results are tabulated in Table 4. The mean value and standard deviation of the activation energies for both the samples are presented in Table 4, which showed that the nanoparticle-induced mixed surfactant system had a higher value of the activation energy (39.131 kJ/mol) compared to the surfactant system without nanoparticles (33.365 kJ/mol). This high value points to higher thermal stability of nanofluids and the presence of a 3-D network of micelles involving stronger interactions between macromolecular aggregates than are present in other fluids (Dantas *et al.*, 2003b).

Table 4: Activation energy values for different samples in the temperature range of 303-333K.

S.No	Sample	Mean Value of the Activation Energy, E (kJ/mol)	Std. Deviation
2	34% C/S ALS+SLS, 0.1% NaOH	33.365	0.471
4	34% C/S ALS+SLS, 0.1% NaOH + 500 ppm nano particle	39.131	0.327

Shear Stress vs. Shear Rate

Figure 8 shows the variation of the shear stress (τ , Pa) as a function of the shear rate ($\dot{\gamma}$, s⁻¹) for 34% C/S ALS+SLS with 0 ppm and 500 ppm SiO₂ nanoparticles. The fluid is basically a non-Newtonian fluid and the shape of the flow curves is represented by a power-law equation:

$$\tau = k\dot{\gamma}^n$$

where “ k ” is the consistency index (in N·s/m²), and “ n ” is the dimensionless flow behavior index. This equation is also called the Ostwald–de Waele relationship (Goel *et al.*, 2002). Table 5 shows the mean values and standard deviation values of the power law parameters calculated manually using the shear stress and shear rate data for 34% C/S ALS+SLS +0.1% NaOH with 0% and 500 ppm SiO₂ nanoparticles. It can be seen that all “ n ” values are less than 1, representing a pseudoplastic nature and the plots of shear rate vs. shear stress are concave downward, which also represents a pseudoplastic behavior, i.e., shear thinning nature. A near power law plot was obtained for 34% C/S ALS+SLS, 0.1% NaOH + 500 ppm nanoparticle ($R^2=0.9553$ with standard error of 0.257), while the plot for 34% C/S ALS+SLS, 0.1% NaOH shows a certain deviation from the power law model ($R^2=0.837$ with standard error of 0.400). The coefficient values with their standard error of estimate are presented in Table 6.

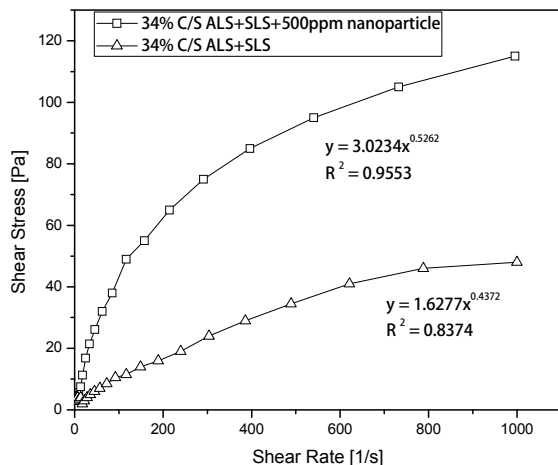


Figure 8: Variation of shear stress vs. shear rate for 34% SLS+ALS with and without nanoparticles.

To test the difference between theoretical and experimental power law parameters, the t-test was performed and the results are tabulated in Table 7. The Levene test for 'k' and 'n' was performed to determine the quality variances and significance values. It

can be observed from the table that the significance value is equal to 0.000 which is less than $p=0.05$, i.e., the assumption of equality of variances for the t-test is violated. Therefore, "Equal variances not assumed" t-statistics is considered in the Table 7. Since the significance values of the power law parameters "n" and "k" for both the samples are greater than 0.05 [0.360 (n_1), 0.620(k_1), 0.681(n_2) and 0.146(k_2)], the power law model is validated by all the experimental data.

Dynamic Oscillatory Measurements

Dynamic Oscillatory experiments measure the linear viscoelastic response of materials and are known to be the most valuable probes of gel or network structure. Steady shear measurements accurately represent the process conditions and oscillatory measurements are necessary for an insight into the numbers of network crosslinks. Linear Viscoelastic measurements can be used to determine the crosslink density of the gel, the kinetics of gel formation and shear degradation of the gel structure (Goel *et al.*, 2002).

Table 5: Values of k and n for different SBG.

S.No	Sample	Value of flow behavior index, n			Value of consistency index, k		
		Mean value	Std. deviation	Theoretical value	Mean value	Std. deviation	Theoretical value
1.	34% C/S ALS+SLS	0.508	0.346	0.437	1.965	3.062	1.627
2.	34% C/S ALS+SLS + 500 ppm SiO ₂	0.490	0.414	0.526	4.237	3.858	3.023

Table 6: Coefficient table with standard error and significance value for 34% C/S ALS+SLS+0.1% NaOH with 0 and 500 ppm SiO₂.

34% C/S ALS+SLS+0.1% NaOH		Unstandardized Coefficients		Significance
		B	Std. Error	
For 0 ppm SiO ₂				
n_1		0.437	0.036	0.000
k_1		1.628	0.236	0.000
For 500 ppm SiO ₂				
n_2		0.526	0.040	0.000
k_2		3.023	0.490	0.000

Table 7: Independent t-test for Power law parameters of 34% C/S ALS+SLS +0.1% NaOH with 0 and 500 ppm SiO₂ nanoparticles.

Sample	Parameter		Levene's Test for Equality of Variances	t-test for Equality of Means	
			Significance	Degree of freedom	Significance (2-tailed)
34% C/S ALS+SLS +0.1% NaOH	n_1	Equal Variances Assumed	0.000	47	0.283
		Equal Variances not Assumed		20.000	0.360
	k_1	Equal Variances Assumed	0.000	47	0.562
		Equal Variances not Assumed		20.000	0.620
34% C/S ALS+SLS +0.1% NaOH+500 ppm SiO ₂	n_2	Equal Variances Assumed	0.000	47	0.660
		Equal Variances not Assumed		20	0.681
	k_2	Equal Variances Assumed	0.000	47	0.115
		Equal Variances not Assumed		20.000	0.146

Figures 9-10 show the variation of the storage modulus [$G'(\omega)$] and loss modulus [$G''(\omega)$] with respect to frequency from 1 to 100 s^{-1} at 40 °C. Oscillatory shear measurements were made for 34% C/S ALS+SLS system, and for the effect of addition of nanoparticles on the same.

For all samples, the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, were almost independent of the angular frequency range since the curves are almost parallel to the x-axis, which show basically the gel nature. The storage modulus always maintained a higher value than the loss modulus, indicating the viscoelastic nature of the fluid where elasticity is dominant.

The nanoparticle-induced mixed surfactant system exhibited higher values of $G'(\omega)$ and $G''(\omega)$ as compared to the gel without nanoparticles. The presence of nanoparticles leads to stronger interactions between the macromolecular aggregates and a 3-D network of worm-like micelles is formed in the fluid.

The frequency where $G'(\omega) = G''(\omega)$ (crossover point) is referred to as the relaxation time of the network. In both the samples, no crossover of $G'(\omega)$ and $G''(\omega)$ was observed within the frequency range under investigation (1–100 s^{-1}). This means that the crossover point must have been below 1 s^{-1} , indicating good capacity of the fluid to suspend the particles, because the lower the crossover frequency, the higher the particle suspension capability (Gaillard *et*

al., 2013). Also, recent studies have shown that fluids having a minimum viscosity value of 25 cP (at 100 s^{-1}) and elastic modulus of 2 Pa are good enough to suspend proppant for hydraulic fracturing (Thampi *et al.*, 2014). In the present case, both the samples had an elastic modulus value much higher than 2 Pa and viscosities above 100 cP.

Miscibility Test

The breaking characteristic of fracturing fluid was examined by carrying out miscibility tests for VES fluids in the presence of water. The viscosity of gel-water mixtures at different proportions is presented in Figures 10 and 11 as a function of temperature. The results show that the highly viscous gel is completely miscible with water and breaks into a low viscous liquid. This occurs as the worm-like micelles break into non-viscous, more spherical micelles, which can no longer form a network (Nasr-El-Din *et al.*, 2003). Also by adding water to the gel, the surfactant concentration eventually falls to a level at which insufficient numbers of micelles are present to entangle and the viscosity decreases. Higher viscosity values were obtained at 2:1 and 3:1 ratios, which indicate that the gel is broken to a lesser extent, but presented a low viscosity at increased temperature. The nanoparticle-induced mixtures also behave similarly. These results clearly indicate that VES fluid does not need any breaker for cleaning of the formation after fracturing.

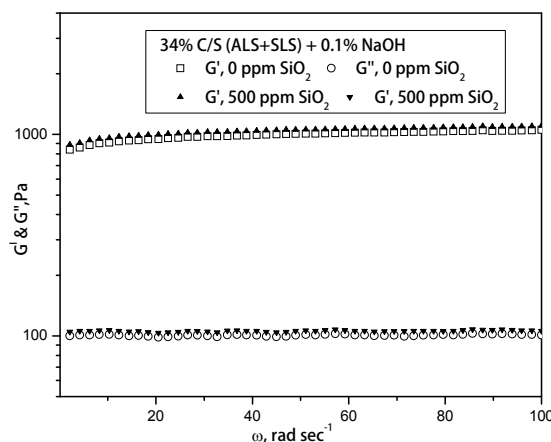


Figure 9: Variation of the storage (G') and loss (G'') moduli with frequency (ω) for 34% C/S ALS+SLS + 0.1% NaOH for 0 ppm and 500 ppm SiO_2 nanoparticles at 40 °C.

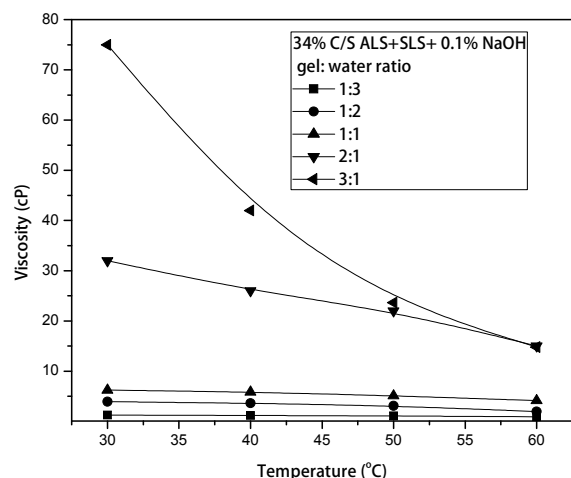


Figure 10: Variation of the viscosity with temperature for different gel –water ratios for 34%C/S ALS+SLS+0.1% NaOH.

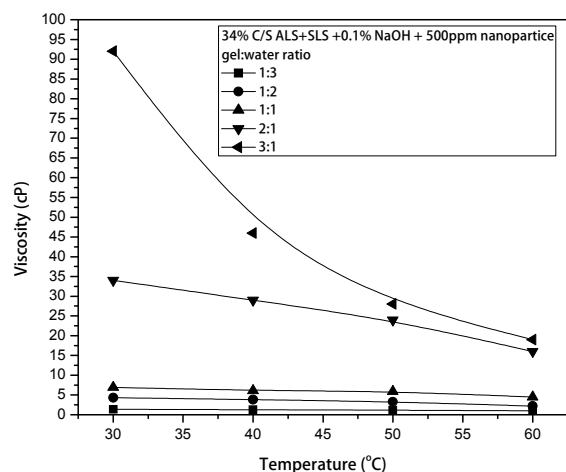


Figure 11: Variation of the viscosity with temperature for different gel –water ratios for 34%C/S ALS+SLS+0.1% NaOH + 500 ppm SiO₂ nanoparticles.

CONCLUSIONS

In the present work, surfactant-based gels (VES) were synthesized with anionic surfactants, i.e., ammonium lauryl sulfate (ALS) and sodium lauryl sulfate (SLS). The rheology of the prepared gels shows shear thinning behavior with a prominent viscoelastic nature. Elasticity is predominant, which helps the proppant carrying capacity. Addition of NaOH improves the viscosity of the gel to a certain extent because of an increase in the micelle population in the basic medium. It could also be concluded from the results that a mixture of ALS and SLS provides a better gel system with higher viscosity compared to

the individual surfactants. The VES gel also shows good miscibility in all proportions with water, thus nullifying the probability of formation of damage without the aid of any breaker. This prepared gel is thermally stable up to 70 °C and can be effectively used to fracture low temperature reservoirs like CBM.

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