

Viscosity of the oil-in-water Pickering emulsion stabilized by surfactant-polymer and nanoparticle-surfactant-polymer system

Tushar Sharma^{1,2}, G. Suresh Kumar¹, Bo Hyun Chon³ and Jitendra S. Sangwai^{1,*}

¹*Petroleum Engineering Program, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai 600036, India*

²*School of Petroleum Technology, Pandit Deendayal Petroleum University, Gandhinagar 382007, India*

³*Department of Energy Resources Engineering, Inha University, Incheon 402-751, Republic of Korea*

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Information on the viscosity of Pickering emulsion is required for their successful application in upstream oil and gas industry to understand their stability at extreme environment. In this work, a *novel* formulation of oil-in-water (o/w) Pickering emulsion stabilized using nanoparticle-surfactant-polymer (polyacrylamide) system as formulated in our earlier work (Sharma *et al.*, Journal of Industrial and Engineering Chemistry, 2014) is investigated for rheological stability at high pressure and high temperature (HPHT) conditions using a controlled-strain rheometer. The nanoparticle (SiO₂ and clay) concentration is varied from 1.0 to 5.0 wt%. The results are compared with the rheological behavior of simple o/w emulsion stabilized by surfactant-polymer system. Both the emulsions exhibit non-Newtonian shear thinning behavior. A positive shift in this behavior is observed for surfactant-polymer stabilized emulsion at high pressure conditions. Yield stress is observed to increase with pressure for surfactant-polymer emulsion. In addition, increase in temperature has an adverse effect on the viscosity of emulsion stabilized by surfactant-polymer system. In case of nanoparticle-surfactant-polymer stabilized o/w emulsion system, the viscosity and yield stress are predominantly constant for varying pressure and temperature conditions. The viscosity data for both o/w emulsion systems are fitted by the Herschel-Bulkley model and found to be satisfactory. In general, the study indicates that the Pickering emulsion stabilized by nanoparticle-surfactant-polymer system shows improved and stable rheological properties as compared to conventional emulsion stabilized by surfactant-polymer system indicating their successful application for HPHT environment in upstream oil and gas industry.

Keywords: Pickering emulsion, nanoparticle, polyacrylamide, surfactant, rheology

1. Introduction

The unceasing decline in oil recovery of conventional resources has raised the need of developing new technologies that can recover additional oil from the existing reservoirs or so far un-swept areas. Chemical enhanced oil recovery (EOR) that uses a chemical slug blended with suitable chemicals (alkali, surfactant and polymer) has been widely exercised and observed to be a potential tool to recover oil from deep hard-to-produce reservoirs where the viscosity of crude oil is significantly higher than that of conventional oil (Pei *et al.*, 2012). One of the solutions is to use oil in water (o/w) emulsion as a promising tool to enhance the recovery of oil from un-swept zone due to its appealing rheological characteristics. However, o/w emulsion stabilized *solely* by conventional emulsifiers could not find suitable implementation in the oilfield due to destabilization and deformed rheological behavior at high temperature (Binks and Rocher, 2009; Pons *et al.*, 1995). In general, the temperature has disruptive effect on the rheological properties of emulsion due to increase in

the average droplet size of dispersed phase (Dickinson and Pawlowsky, 1996), conveying unsuccessful penetration of droplets into the oil reservoirs. This demands the inquest for a new emulsion system for a successful EOR application. Pickering emulsions stabilized using surfactant and colloidal particles such as nanoparticles are gaining wider recognition in petroleum industry due to their high strength, self-standing capability and stabilized flow behavior.

Polyacrylamide (PAM) is a water soluble polymer and is widely used in several oilfield applications such as viscosity enhancer, drilling fluid design and in EOR application due to its favorable rheology, compatibility with other chemicals and cost-effectiveness (Thomas *et al.*, 2012). The PAM together with surfactant molecules can attach at the oil-water interface during emulsification forming a steric barrier against droplet deformation, thereby suggesting long term stability suitable for oilfield implementation (Meister *et al.*, 1976). In order to select a successful fluid for chemical EOR, the polymer partially hydrolyzed polyacrylamide (HPAM) shows considerable development in rheological properties depending on the polymer concentration and molecular weight (Wu, 2013; Jung *et al.*, 2013). It has been investigated that the stable nanofluids

*Corresponding author: jitendrasangwai@iitm.ac.in

can be prepared using another oilfield biopolymer, xanthan gum, increasing the viscosity of continuous phase and can be utilized for high pressure and high temperature (HPHT) oilfield applications (Ponmani *et al.*, 2014; William *et al.*, 2014).

Stable rheology and long term stability are prerequisite for successful use of o/w emulsion. It is observed that the rheological properties of surfactant based emulsions is improved with the help of co-surfactants such as hydrophobically modified alkali-swelling emulsion (HASE) polymer (English *et al.*, 2002). The formulation, stability and rheological properties of o/w emulsion and colloidal suspensions stabilized by surfactant or nanoparticles have been published in ample literatures with suitable comparisons (Wolf *et al.*, 2007; Frith *et al.*, 2008; Kim and Kim, 2012; Ozel *et al.*, 2014). In addition, several studies reported other important aspects related to emulsion characterization such as emulsion type (Lequeux, 1998), viscoelastic properties (Lequeux, 1998), interfacial tension measurements (Perino *et al.*, 2013), interfacial rheology (Perino *et al.*, 2013; Erni *et al.*, 2007), droplet size distribution (Wolf *et al.*, 2007; Kundu *et al.*, 2013), temperature effect on emulsion properties (Kundu *et al.*, 2013) and heavy oil emulsion system (Steinborn and Flock, 1983). However, the above studies have been conducted at normal pressure and temperature conditions. Indeed, for a stable o/w emulsion, the strength of the 3D network formed due to the synergistic interaction of emulsifiers at the oil-water interface at an elevated temperature and pressure is a key factor in explaining the stability and viscoelastic behavior at hostile reservoir conditions.

Few researchers have investigated the effect of high pressure (up to 100 MPa) and high temperature (400 K) on the rheological behavior of invert emulsion mud and bentonite mud system, respectively (Houwen, 1986; Alderman *et al.*, 1988). Well-known rheological model fitting the rheology data is reported with relevant advantages of using the same at downhole HPHT conditions. Subsequently, few other studies on the stability and rheological behavior of conventional fluids and emulsion systems at HPHT conditions are reported. Dickinson and James (1999) observed that the high pressure environment (200-800 MPa) can reduce the flocculation of o/w emulsion (containing β -lactoglobulin and a nonionic surfactant) with significant improvement in the stability and rheology of the system. Industrially applicable conventional systems like xanthan fluids (Sani and Shah, 2001; Ponmani *et al.*, 2014) have suggested improved stability of the system at HPHT conditions due to excellent pressure induced control over the destabilization process.

In spite of several published studies on the rheological behavior of conventional o/w emulsion, the studies related to HPHT rheology of o/w Pickering emulsions have not been completely understood. Binks *et al.* (2005) investi-

gated the stability and rheological behavior of bentonite clay particle stabilized emulsions. They observed that clay particle results in the formation of highly structured tactoids due to the formation of an integrated network of clay tactoids and droplets suggesting the possible interaction between dispersed particles and oil droplets. Zhang *et al.* (2010) reported the studies on the rheological characteristics and advantages associated with the use of SiO₂ nanoparticle stabilized o/w emulsion for the enhanced oil recovery than conventional emulsions stabilized solely by surfactant. In general, the occurrence of droplet coalescence, decrease in viscosity and loss in rheological properties at HPHT environment for conventional o/w emulsions can be promoted significantly by the use of high molecular weight polymer, surfactant and nanoparticles *synergistically*. The successful implementation of nanoparticle stabilized Pickering emulsion for EOR application demands for the focused investigations on the emulsion stability and rheology at HPHT conditions.

In our recent work, the use of water soluble polymer PAM along with nanoparticle and surfactant have shown the formation of thermally stable o/w Pickering emulsion stabilized by nanoparticle-surfactant-polymer system (Sharma *et al.*, 2014). This work presents the investigations on the viscosity of this *novel* o/w Pickering emulsion at various conditions of pressure and temperature suitable for EOR applications. The results are compared with the rheological behavior of simple o/w emulsion stabilized by surfactant-polymer system. We report the information on the viscosity of these system with the effect of subsurface equivalent pressure (0.1 to 30 MPa) and temperature (298 to 371 K). The surfactant-polymer (henceforth referred to as surfactant stabilized emulsion, unless specified) and nanoparticle-surfactant-polymer (henceforth referred to as nanoparticle stabilized emulsion, unless specified) o/w emulsion system contains an oilfield polymer polyacrylamide (PAM), surfactant, sodium dodecylsulfate (SDS, 0.22 wt%) and nanoparticles, *viz.*, hydrophilic SiO₂ (~15 nm diameter) and partially hydrophobic clay (<80 nm diameter) with varying concentrations of 1.0 to 5.0 wt%.

2. Materials and Methods

2.1. Materials

Deionized water is obtained from Millipore® Elix-10 purification apparatus and is used in all experiments. The oil is purchased from a commercial retail outlet of Hindustan Petroleum Corporation Ltd., India. The supplied oil is lubricating oil with a flash point of around 488 K and density 0.97 gm/cc. Nanoparticles, *viz.*, hydrophilic SiO₂ (~15 nm diameter) and partially hydrophobic clay (<80 nm diameter) are purchased from Sisco Research Laboratories, India. An oilfield polymer polyacrylamide (molecular weight of 10⁷ g/mol), purchased from SNF Floerger, France,

is used as received. The surfactant SDS is purchased from Ranbaxy Fine Chemicals Ltd., India. All solutions are prepared by using an accurate analytical weighing balance (Reptech® RA-1012 with a repeatability of ± 0.0001 mass fraction) and a homogenizer (Remi® RQT-127/D) with mixing speed ranges from 300 to 6000 rpm.

2.2. Formulation of Pickering emulsion

Two types of o/w emulsion systems, one stabilized by surfactant-polymer and the other stabilized by nanoparticle-surfactant-polymer system are investigated to study the effect of high pressure and high temperature on the rheological behavior. A typical concentration of 1000 ppm of polymer PAM is selected from preliminary investigations on the thermal stability of emulsion prepared using varying concentration and is used as a base polymer solution for the formation of all o/w emulsions. A conventional detergent (ingredients such as, 5-15% anionic surfactants; oxygen-based bleaching agents, viz., <5% non-ionic surfactants, phosphonates, polycarboxylates; and zeolites) is mixed with SDS (HLB=40) in the ratio of 57:43, respectively, to get HLB of 9.98 close to that of oil (HLB=10). Aqueous solution of the surfactant and polymer is prepared by mixing surfactant in a stock 1000 ppm polymer solution and stirred for 30 min to accelerate the dissolution of surfactant. Critical micelle concentration (CMC) of 0.20 wt% for the mixed dispersion of surfactant-polymer is determined by surface tension measurement using spinning drop video tensiometer (SVT 20N, Data Physics®, Germany). In order to ensure the formation of surfactant micelles in an optimum quantity, a surfactant concentration slightly higher than CMC (CMC+10% of CMC=0.22 wt%) corresponding to 1000 ppm polymer solution is used for the study. The surfactant-polymer emulsion is prepared mechanically by homogenizing the oil with mixed dispersion of surfactant and polymer. To prepare nanoparticle-surfactant-polymer o/w emulsion, nanoparticles such as SiO₂ and clay of varying concentration from 1.0 to 5.0 wt% are used and added accordingly to surfactant-polymer o/w emulsion. Homogenizer with a constant speed of 3000 rpm for 1 h is used for the preparation of o/w emulsion. The dispersed phase (*i.e.*, oil) concentration of all the emulsions is kept as 0.25 volume fraction (Sharma *et al.*, 2014).

2.3. Measurement of viscosity

The measurements on the viscosity of o/w emulsion are performed using a controlled-strain compact rheometer MCR 52 (Anton Paar®, Physica, Austria) equipped with essential units to maintain the desired condition of the pressure and temperature as shown in Fig. 1. The set-up is similar to the one used in our earlier studies on the rheological measurements of polymerizing system (Sangwai *et al.*, 2006 and 2007). The temperature of the sample is

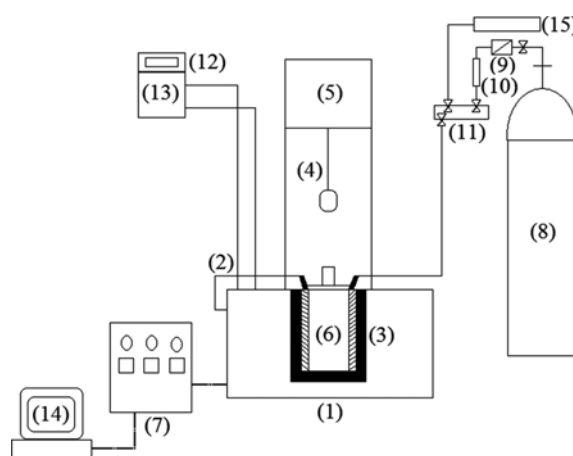


Fig. 1. Schematic of the experimental set-up used for the measurement of viscosity of emulsion. 1: High pressure high temperature compact rheometer; 2: Temperature and pressure sensor; 3: Thermal jacket; 4: Magnetic coupling; 5: measuring head; 6: Pressure cup; 7: Data acquisition unit; 8: Gas cylinder; 9: Anti freezing gas heater; 10: Pressure regulator; 11: Pressure valves assembly; 12: Temperature control unit; 13: Escy® circulator bath; 14: Computer; and 15: Hydraulic pump unit.

controlled automatically with the use of in-built Peltier system. The rheometer is well armored with a pressure cell (working range from 0.1 to 40 MPa) consisting of a magnetic coupling. The data on the viscosity for varying shear rate is measured using electronically commutated synchronous motor system in the temperature and pressure range of 298 to 371 K and 0.1 to 30 MPa, respectively. The measurements are repeated at least three times for each experiment to confirm the repeatability. Pressure cell is properly cleaned and dried and the o/w emulsion samples are mildly agitated to homogenize the dispersed phase before the measurement. Before the start of the experiment, each pressurized sample is allowed to be thermally stable at desired temperature for about 10 min. The interfacial deposition of nanoparticles is also confirmed by a scanning electron microscope (SEM) study (ZEISS® Ultra-55, Germany). Prior to the SEM study, the freeze emulsion samples are placed to cover glasses carefully. The cover glasses with individual samples are attached to aluminum stubs with adhesive taps and examined using a scanning electron microscope (Saha *et al.*, 2011).

3. Results and Discussion

In this section, results on the viscosity of a surfactant-polymer and nanoparticle-surfactant-polymer stabilized o/w emulsions are presented. The results on the characterization of these emulsions using SEM studies are also discussed correlating the relevance to the rheological behavior of these emulsions.

3.1. Characterization of o/w emulsions

The surfactant-polymer and nanoparticle-surfactant-polymer stabilized o/w emulsions are prepared by mixing 0.22 wt% of surfactant mixture in 1000 ppm polymer aqueous solution with desired concentration of nanoparticle. Here, the polymer PAM acts as a thickener to slow down the rate of creaming by increasing the emulsion viscosity. The rate of creaming is found to be more for surfactant-polymer stabilized emulsion than emulsion system formed with nanoparticle-surfactant-polymer (Sharma *et al.*, 2014). In case of surfactant-polymer stabilized o/w emulsion, the average droplet diameter is determined just after the emulsification using a particle size analyzer (Zetasizer Nano-S90, Malvern Instruments, UK) and is observed to be about 6 to 7 μm . The average droplet diameter for 1.0 wt% SiO_2 stabilized emulsion is observed to be in the range of 2 to 2.5 μm at the end of 23 days after emulsification. In addition to SiO_2 nanoparticle, clay nanoparticle also stabilized the emulsion by diminishing the rate of droplet coalescence. The DLS analysis indicates that the average droplet size for 1.0 wt% clay stabilized emulsion system is observed to be 3.65 μm at the end of 23 days after emulsification and the corresponding emulsion remained stable for several days (Sharma *et al.*, 2014). For nanoparticle-surfactant-polymer stabilized emulsions, the average droplet diameter does not increase convincingly with time even after 2 months (Sharma *et al.*, 2014). In general, the droplets of nanoparticle-surfactant-polymer stabilized o/w emulsions are smaller in size and coalescence stable as compared to the surfactant-polymer stabilized emulsions, thus the former are expected to penetrate easily in subsurface reservoirs without much retention and subsequently, it will help in improving the resultant oil recovery.

3.2. Viscosity of polyacrylamide aqueous solution

Viscosity of polyacrylamide aqueous solution is investigated at high pressure (0.1 to 30 MPa) and high temperature (298 to 371 K) conditions in the absence of surfactant and nanoparticles and used for comparison with the rheological studies on the surfactant-polymer and nanoparticle-surfactant-polymer stabilized o/w emulsion system. Fig. 2a shows flow profiles for the effect of pressure on the viscosity of PAM aqueous solution. It is observed that the polymer solution behaves as a non-Newtonian shear thinning fluid over the complete range of shear rates concurring with literature studies (Pal, 1992). The viscosity and non-Newtonian shear thinning behavior are observed to be promoted with increase in the pressure above 0.1 to 5, 10, 20 and 30 MPa as shown in Table 1 and Fig. 2a. The viscosity increases from 1.01 Pa·s at 0.1 MPa to about 86 Pa·s at 10 MPa and ceases to vary with further increase in pressure up to 30 MPa. The increase in viscosity of pure PAM aqueous solution with pressure can be due to the possible pressure induced polymer molecular association (entanglements of the polymer molecules) in an aqueous phase. It is speculated that the molecules come closer with increase in the system pressure inhibiting the Brownian motion of the molecules and thus, increasing the viscosity. The effect of temperature is also observed on the rheological behavior of PAM aqueous solution. The viscosity of PAM aqueous solution is observed to decrease (see Table 1 and Fig. 2b) with increase in temperature above 298 K for all pressure conditions (0.1 to 30 MPa). The effect of temperature on the viscosity at high pressure conditions of 10 MPa and above remains almost the same. The viscosity data for simple PAM polymer solutions (Fig. 2a) are fitted satisfactorily with a well-known Car-

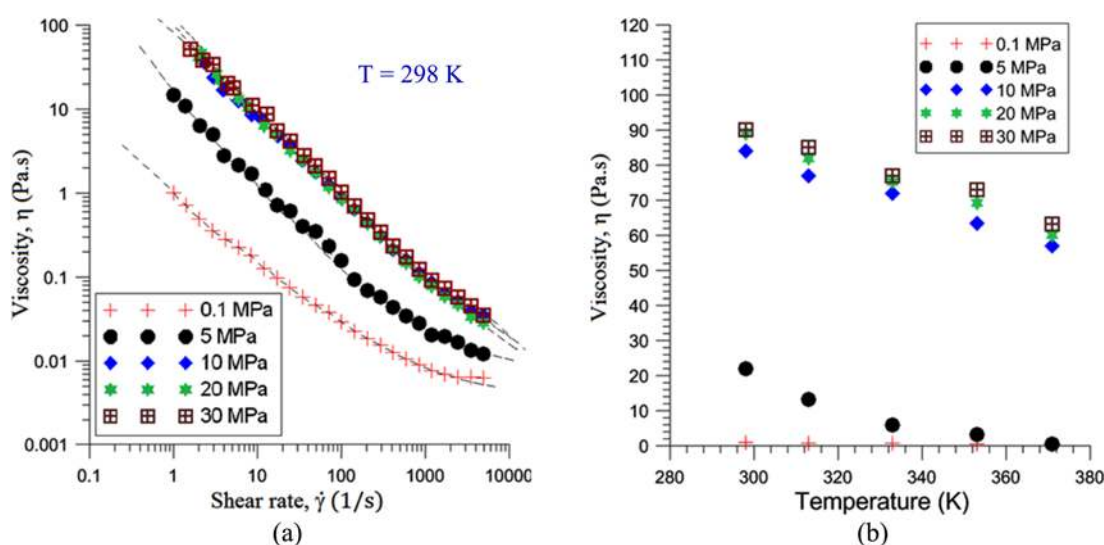


Fig. 2. (Color online) Effect of pressure (0.1 to 30 MPa) and temperature (298 to 371 K) on the rheological behavior of pure 1000 ppm polymer aqueous solution. Dash line shows predictions of the Carreau model.

Table 1. Details on the viscosity of PAM polymer aqueous solution as a function of pressure and temperature^a.

| Sample | Concentration ppm | 0.1 MPa | | 5 MPa | | 10 MPa | | 20 MPa | | 30 MPa | |
|--------------------------------|----------------------|---------|---------------|-------|---------------|--------|---------------|--------|---------------|--------|---------------|
| | | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) |
| Polymer aqueous solution | 1000 | 298 | 1.01 | 298 | 22 | 298 | 85.8 | 298 | 89 | 298 | 88 |
| | | 313 | 0.817 | 313 | 13.2 | 313 | 77 | 313 | 82 | 313 | 85 |
| | | 333 | 0.613 | 333 | 5.98 | 333 | 72 | 333 | 75.3 | 333 | 77 |
| | | 353 | 0.468 | 353 | 3.21 | 353 | 63.5 | 353 | 69.2 | 353 | 73 |
| | | 371 | 0.324 | 371 | 0.486 | 371 | 57 | 371 | 60.1 | 371 | 63.2 |

^aT=temperature, η =viscosity (at shear rate of 1.0 s⁻¹)

reau model with correlation ratio (R^2) ranges from 0.95 to 0.99 as shown below (Pal, 1992; Sani and Shah, 2001):

$$\eta_{eff} = \frac{\eta_0 - \eta_{inf}}{\{1 + (a\dot{\gamma})^2\}^p} + \eta_{inf}; \quad \eta_0 - \eta_{inf} > 0, \quad (1)$$

where η_{eff} denotes the viscosity at the given shear rate $\dot{\gamma}$, η_0 and η_{inf} are the viscosities at zero and infinite shear rates (Pa·s), respectively. a is the relaxation time (s) and p is a constant.

3.3. Viscosity of surfactant-polymer stabilized o/w emulsion

The viscosity of the surfactant-polymer stabilized o/w emulsions are investigated at high pressure (0.1 to 30 MPa) and high temperature (298 to 371 K) conditions and shown in Fig. 3. At low pressures (0.1 and 5 MPa), o/w emulsions stabilized by surfactant-polymer system are observed to show gradual decrease in the viscosity with increase in shear rate as shown in Fig. 3a. On the other

hand, the increase in pressure above 5 MPa (at 298 K) leads to the significant increase in the viscosity of emulsion from 0.21 Pa·s at 5 MPa to about 47 Pa·s at 10 MPa (see Table 2). This behavior is consistent for the viscosity data at 20 and 30 MPa as well. The increase in emulsion viscosity with increase in pressure (above 5 MPa) may be due to the pressure induced droplet flocculation (Dickinson and Pawlowsky, 1996). In addition, at high pressure of 10 MPa and above, viscosity vs. shear rate data showed rapid decrease in the viscosity with shear rate showing stringent non-Newtonian shear thinning behavior as compared to the flow curves at low pressure conditions of 0.1 MPa and 5 MPa (Fig. 3a). It is also observed that the viscosity of surfactant-polymer stabilized o/w emulsion is lower than that of pure aqueous PAM solution. For example, the near-zero shear viscosity of the emulsion is observed to be 0.19 Pa·s at 0.1 MPa (Table 2), which is otherwise observed to be 1.01 MPa at the same pressure for pure PAM solution (see Figs. 2a, and 3a). This reduction in vis-

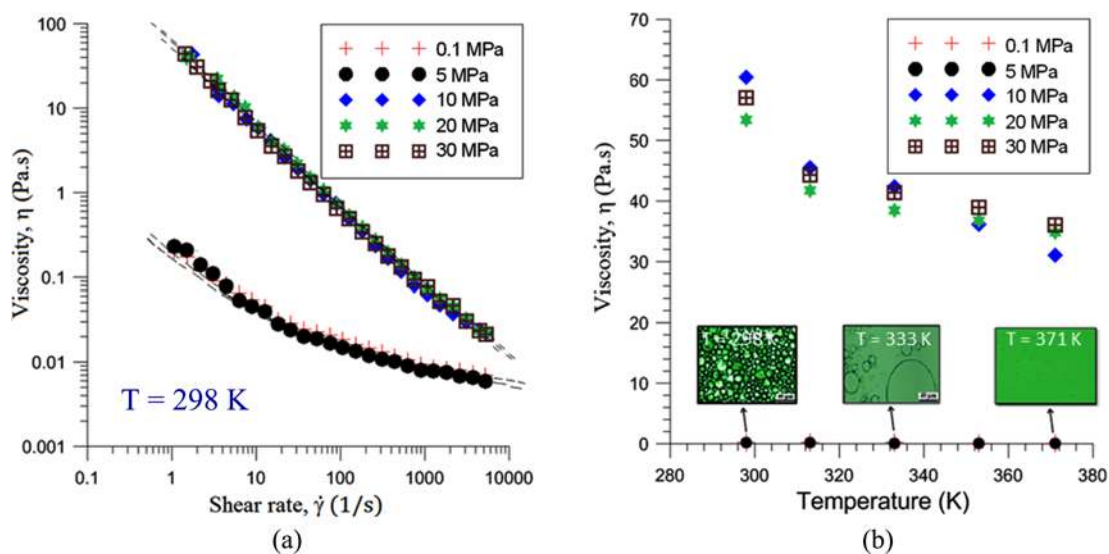


Fig. 3. (Color online) Flow profiles and the effect of (a) high pressure (0.1 to 30 MPa) and (b) high temperature (298 to 371 K) on the viscosity of surfactant-polymer stabilized o/w emulsion. The microscopic insets in (b) show the droplet deformation due to coalescence with increase in temperature. Dash line shows the predictions of the Herschel–Bulkley model.

Table 2. Details on the viscosity of surfactant-polymer o/w emulsion as a function of pressure and temperature.

| Sample | Concentration ppm | 0.1 MPa | | 5 MPa | | 10 MPa | | 20 MPa | | 30 MPa | |
|--|------------------------------|---------|---------------|-------|---------------|--------|---------------|--------|---------------|--------|---------------|
| | | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) |
| Surfactant- polymer o/w emulsion | SDS=0.22 wt% PAM=1000 ppm | 298 | 0.194 | 298 | 0.212 | 298 | 47 | 298 | 45.4 | 298 | 47 |
| | | 313 | 0.111 | 313 | 0.185 | 313 | 45.5 | 313 | 41.7 | 313 | 44.3 |
| | | 333 | 0.114 | 333 | 0.110 | 333 | 42.4 | 333 | 38.4 | 333 | 41.4 |
| | | 353 | 0.102 | 353 | 0.103 | 353 | 36.1 | 353 | 36.72 | 353 | 39 |
| | | 371 | 0.090 | 371 | 0.091 | 371 | 31 | 371 | 34.8 | 371 | 36 |

cosity of surfactant-polymer stabilized o/w emulsion than pure PAM solution may be attributed to the combined effect of surfactant on the PAM molecules in lowering the entanglements due to the formation of mixed surfactant-polymer micelles (English *et al.*, 2002) and also to the elongation of oil droplets as the shear rate increases. The in-situ movement of polymer molecule in the emulsion system at low and high pressure may not be known explicitly. However, it is expected that, at relatively lower reservoir pressure, the mean molecular distance between the emulsion droplets and polymer molecules are relatively higher (independent and less flocculated) and subsequently yields a low viscosity emulsion associated with the emulsion droplet interfaces. However, when the pressure is relatively high, then the mean molecular distance between the fluids particles are relatively low (intact and densely flocculated) and consequently leads to a solution that behaves as a continuous phase with higher viscosity (Dickinson and Pawlowsky, 1996). This is physically reasonable concept for liquids, while the same does not hold good for gases.

Fig. 3b shows the effect of temperature on the viscosity (at different pressure conditions) and droplet structure (microscopic insets) for surfactant-polymer stabilized o/w emulsion. It is observed that the viscosity of emulsion decreases with increase in temperature due to the significant augmentation in Brownian motion among the polymer molecules. At 0.1 MPa pressure, the emulsion viscosity decreases from 0.19 Pa·s at 298 K to 0.11 Pa·s at 333 K followed by 0.09 Pa·s at 371 K (see Table 2). The increase in temperature may cause the deformation of surfactant layer around the droplets due to the weakening of intermolecular forces at the oil-water interface. The emulsion is becoming unstable with respect to coalescence and the droplets start converting into larger droplets at the expense of smaller ones, probably due to the change in composition of the continuous phase. The increase in droplet size with increase in temperature above 318 K is visible. Subsequently, the smaller droplets completely disappear and convert into larger ones at a temperature of about 334 K. These observations on the said emulsion system justify their thermally unstable nature as observed in our previous

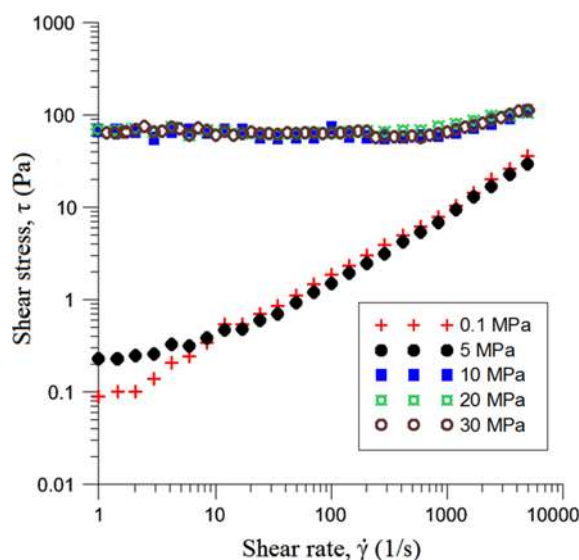
study (Sharma *et al.*, 2014).

The phenomenon of droplet flocculation can also be supported with the observation on yield stress (Pal, 1993). The yield stress for the surfactant-polymer stabilized emulsion system as obtained from stress-sweep test (Fig. 4) is observed to be about 0.09 Pa at 0.1 MPa, which is relatively much less. The yield stress of this emulsion increases drastically with increase in pressure above 5 MPa and reaches to about 70 Pa at 10 MPa (Fig. 4). It is expected that the increase in pressure enhances the interaction of dispersed oil droplets increasing the yield stress. It is to be noted that the error associated with the reproducibility on the viscosity measurements for the surfactant-polymer o/w emulsion system lies in the range of ± 3.3 to 8.1% of the mean value.

The viscosity data (Fig. 3a) for surfactant-polymer stabilized emulsion system is fitted using a well-known Herschel–Bulkley model with R^2 lies in the range of 0.97 to 0.99 (Pal, 1992; Sani and Shah, 2001):

$$\tau = \tau_0 + b \dot{\gamma}^n, \quad (2)$$

where, τ is the shear stress, $\dot{\gamma}$ the shear rate, τ_0 the yield

**Fig. 4.** (Color online) Effect of pressure (0.1 to 30 MPa) on shear stress of surfactant-polymer stabilized o/w emulsion.

stress, b and n are consistency and flow index. The value of flow index gives information on the flowing behavior of fluid in the direction of shear flow. At low pressures (0.1 and 5 MPa) at 298 K, the emulsion behaves as a shear thinning fluid with $\tau_o = 0.087$ Pa, $n = 0.76$ at 0.1 MPa and $\tau_o = 0.312$ Pa, $n = 0.68$ at 5 MPa. As the pressure increases above 5 MPa, the emulsion showed increase in shear thinning behavior with $n = 0.014$ (10 MPa) and $n = 0.01$ (20 MPa). The increment in pressure from 5 MPa to 10 MPa significantly increases the viscosity and shear thinning nature by about 99.54 and 97.94%, respectively. However, with further increase in pressure to 20 MPa, the viscosity and shear thinning nature increase *marginally* by about 1.7 and 28.57%, respectively. In general, the viscosity of emulsion gets affected significantly showing a state of flocculation and coalescence after certain pressure (above 5 MPa) and temperature (above 318 K) conditions as discussed earlier. The study concludes that the o/w emulsion stabilized by surfactant-polymer system does not show the suitability for HPHT environment due to destabilization and loss in the rheological stability.

3.4. Viscosity of Pickering emulsion stabilized by nanoparticle-surfactant-polymer

The viscosity of nanoparticle-surfactant-polymer stabi-

lized o/w emulsion is investigated at high pressure (0.1 to 30 MPa) and high temperature (298 to 371 K) conditions for varying nanoparticle concentration of 1.0, 3.0 and 5.0 wt% and surfactant and polymer concentration of 0.22 wt% and 1000 ppm, respectively. Fig. 5 shows the viscosity vs. shear rate data for the nanoparticle (1.0 wt% SiO₂ and 1.0 wt% clay)-surfactant-polymer stabilized o/w emulsions. It is observed that the addition of nanoparticle to surfactant-polymer stabilized emulsion enhances the viscosity of o/w emulsions due to the deposition of nanoparticle at the oil-water interface (Binks *et al.*, 2005; Wolf *et al.*, 2007). At 0.1 MPa pressure, the addition of 1.0 wt% nanoparticle to surfactant-polymer stabilized emulsion increases the emulsion viscosity from 0.19 Pa·s to 0.71 Pa·s (SiO₂ emulsion) and 0.76 Pa·s (clay emulsion) as given in Table 3. The rheological behavior of these emulsions at high pressure conditions significantly differs from that of surfactant-polymer emulsion. In contrast to surfactant-polymer stabilized emulsion, these emulsions showed a stable non-Newtonian shear thinning behavior at all pressure conditions (0.1 to 30 MPa). In addition, the nanoparticle-surfactant-polymer stabilized emulsion system using 1.0 wt% SiO₂ and 1.0 wt% clay did not show significant increase in the viscosity with increase in pressure (Fig. 5) as compared to the surfactant-polymer stabilized emulsion

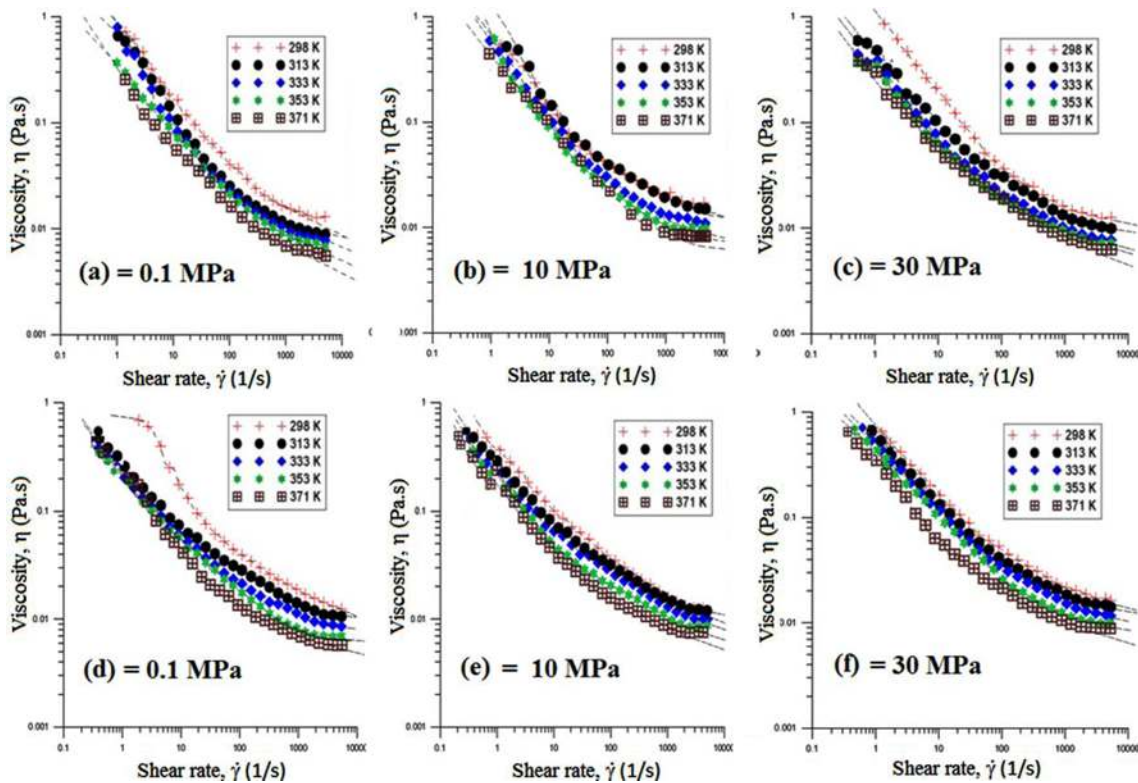


Fig. 5. (Color online) Effect of high pressure (0.1 to 30 MPa) and high temperature (298 to 371 K) on the flow curves of nanoparticle-surfactant-polymer stabilized o/w emulsions. (a-c): 1.0 wt% SiO₂; (d-f): 1.0 wt% clay emulsion system. Dash line shows the predictions of the Herschel–Bulkley model.

Table 3. Viscosity data for nanoparticle-surfactant-polymer o/w emulsions as a function of pressure and temperature.

| Sample | Concentration | 0.1 MPa | | 10 MPa | | 30 MPa | |
|---------------------------|---|---------|---------------|--------|---------------|--------|---------------|
| | | T (K) | η (Pa·s) | T (K) | η (Pa·s) | T (K) | η (Pa·s) |
| SiO ₂ emulsion | SiO ₂ =1.0 wt% SDS=0.22 wt% PAM=1000 ppm | 298 | 0.712 | 298 | 0.728 | 298 | 0.763 |
| | | 313 | 0.812 | 313 | 0.722 | 313 | 0.674 |
| | | 333 | 0.667 | 333 | 0.697 | 333 | 0.666 |
| | | 353 | 0.660 | 353 | 0.701 | 353 | 0.612 |
| | | 371 | 0.652 | 371 | 0.689 | 371 | 0.624 |
| Clay emulsion | Clay=1.0 wt% SDS=0.22 wt% PAM=1000 ppm | 298 | 0.761 | 298 | 0.599 | 298 | 0.719 |
| | | 313 | 0.666 | 313 | 0.601 | 313 | 0.711 |
| | | 333 | 0.612 | 333 | 0.589 | 333 | 0.715 |
| | | 353 | 0.645 | 353 | 0.592 | 353 | 0.700 |
| | | 371 | 0.600 | 371 | 0.585 | 371 | 0.698 |

(see Table 3 and Fig. 3).

In order to check the suitability of nanoparticle-surfactant-polymer o/w emulsion for EOR application, the effect of temperature on the rheological stability is also analyzed. Fig. 5 also shows the effect of temperature from 298 K to 371 K on the viscosity of nanoparticle-surfactant-polymer stabilized emulsions. It is observed that the viscosity of the emulsions gets affected marginally with increase in temperature (Table 3), which may be attributed to the limited droplet coalescence due to the presence of surfactant that modifies the wettability of nanoparticle as well as adsorption of the nanoparticle at the oil-water interface hindering coalescence (Thijssen *et al.*, 2011; Sharma *et al.*, 2014). The error associated with the reproducibility on the viscosity data for the nanoparticle-sur-

factant-polymer o/w emulsion lies in the range of ± 1.8 to 7.6% of the mean value.

The effect of pressure on the yield stress for these emulsions is shown in Fig. 6. At 0.1 MPa pressure, the nanoparticle-surfactant-polymer stabilized emulsions (1.0 wt% SiO₂ and 1.0 wt% clay stabilized) have yield stress of 0.50 Pa (Fig. 6a) and 0.48 Pa (Fig. 6b), respectively, which is slightly higher than the yield stress of surfactant-polymer stabilized emulsion. It is to be noted here that the shear stress of o/w emulsions stabilized by nanoparticle-surfactant-polymer system is observed to be almost constant over a limited range of shear rate (~ 10 s⁻¹), followed by a steady increase thereafter as shown in Fig. 6 (Binks *et al.*, 2005). In addition, it is observed that the yield stress of these o/w emulsion system did not increase with increase

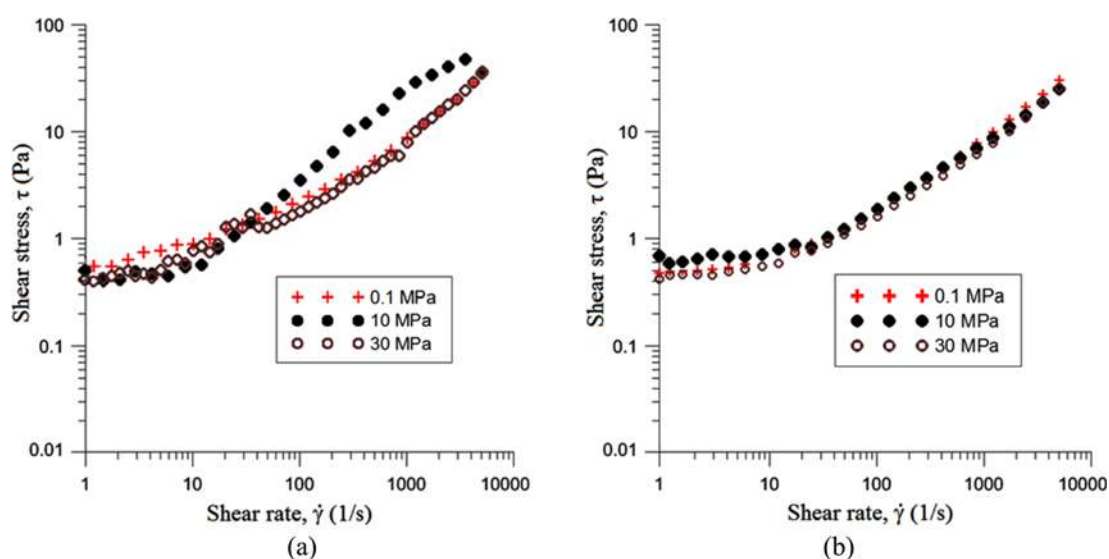


Fig. 6. (Color online) Variation of shear stress with shear rate for o/w emulsions stabilized nanoparticle-surfactant-polymer system at varying pressure (0.1 to 30 MPa) conditions. (a) 1.0 wt% SiO₂ and (b) 1.0 wt% clay.

in the pressure (Fig. 6). This implies that the viscosity and yield stress of nanoparticle-surfactant-polymer emulsion are stable in the pressurized environment. These observations are in-line with the results of Dickinson and Pawlowsky (1996) who carried out studies on the influence of high pressure on the rheological behavior of protein-polysaccharide stabilized emulsion system. The presence of surfactant is expected to change the wettability of nanoparticle to promote their interfacial attachment at the oil-water interface (Lan *et al.*, 2007). We observed that the nanoparticle in the presence of polymer PAM involves in the network modification through the formation of mixed micelles of surfactant along with nanoparticle to create stable o/w emulsion hindering the droplet flocculation (Sharma *et al.*, 2014). To understand and confirm the deposition of nanoparticle aggregates at the droplet surfaces, SEM study of nanoparticle-surfactant-polymer stabilized o/w emulsion is performed. Fig. 7 shows the SEM images for this system. SEM study confirms the morphological characterization and deposition of nanoparticle aggregates at the oil droplet surface as shown in Fig. 7 for 1.0 wt% SiO₂ and 1.0 wt% clay stabilized-surfactant-polymer o/w emulsion system. Oil is represented by dark patches with densely packed nanoparticles multilayer adsorption at the droplet surface. These findings indicate a potential application of nanoparticle-surfactant-polymer emulsion for high pressure applications.

The effect of nanoparticle concentration (> 1.0 wt%) on the viscosity of nanoparticle-surfactant-polymer stabilized o/w emulsion is also investigated. It is observed that with increase in the nanoparticle concentration (*viz.*, 3 and 5.0 wt%), the emulsion viscosity marginally increases and the

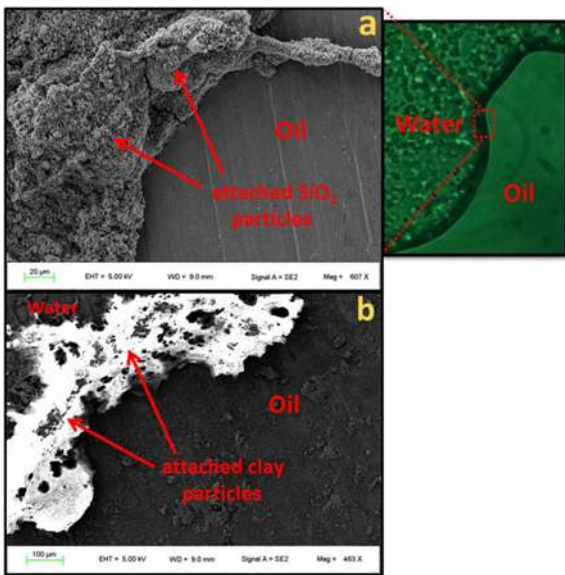


Fig. 7. (Color online) SEM micrographs showing the interfacial layer in nanoparticle-surfactant-polymer stabilized o/w emulsions containing (a) 1.0 wt% SiO₂ and (b) 1.0 wt% clay nanoparticles.

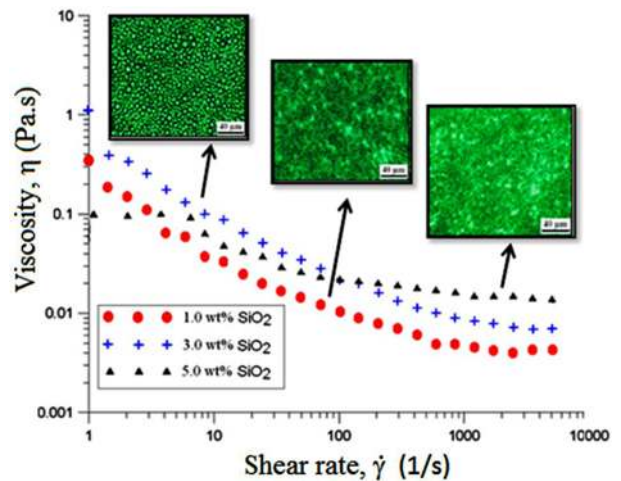


Fig. 8. (Color online) Effect of nanoparticle concentration (1.0 to 5.0 wt%) on the rheological behavior of SiO₂ stabilized o/w emulsion. The microscopic insets show the effect of nanoparticle concentration on droplet structure and size distribution.

structure of droplets converts into clustered form as shown in Fig. 8. The slight increase in the viscosity with increase in nanoparticle concentration can be attributed to the competition of nanoparticle to get adsorbed at the oil-water interface resulting in saturation and, thus marginally affecting the emulsion properties. The droplet clustering due to increase in the nanoparticle concentration is expected to be associated with ‘depletion mechanism’. The depletion mechanism refers to the lowering of osmotic pressure due to the presence of surfactant or polymer, resulting in enhanced nanoparticle attraction at the oil-water interface and causing clustering of nanoparticles (Pal, 1999). Hermes and Clegg (2013) investigated that, in case of Pickering emulsions, the bonds between silica colloids are being broken with increasing deformation and re-formed with shear thickening behavior at large strains due to the presence of surplus particles in the continuous phase. The particle concentration by the surplus particles will play a crucial role during depletion interaction in determining the rate of shear thickening. As pointed out, the rate at which the surplus particles get adsorbed over the droplets resulted from shear thinning will be faster when the particle concentration is relatively high, and subsequently, the rate of shear thickening will be very high and vice-versa. In general, the addition of nanoparticle to surfactant stabilized emulsion in the presence of polymer serves to lower the droplet flocculation and destabilization, making them compatible to apply for chemical EOR techniques at HPHT environment.

The viscosity vs. shear rate data for nanoparticle-surfactant-polymer stabilized emulsions is observed to follow Herschel–Bulkley model (Eq. (2)) with R² lies in the range of 0.97 to 0.99. It is observed that for nanoparticle-sur-

factant-polymer stabilized emulsions, the values of n change marginally with increase in pressure. The corresponding flow index n values for 1.0 wt% SiO₂ stabilized emulsion are 0.83 (0.1 MPa), 0.71 (5 MPa), 0.76 (10 MPa), and 0.78 (20 MPa). For 1.0 wt% clay stabilized emulsion, n values are observed to be as 0.96 (0.1 MPa), 0.80 (5 MPa), 0.80 (10 MPa), and 0.83 (20 MPa). The increment in pressure from 0.1 to 20 MPa represents overall 14.45% (1.0 wt% SiO₂) and 16.66% (1.0 wt% clay) increase in shear thinning behavior, which is significantly less as compared to surfactant-polymer stabilized o/w emulsion.

4. Conclusions

Pickering emulsion shows potential use at high pressure and high temperature applications, particularly for upstream oil and gas industry. The prediction of rheological properties of a Pickering emulsion are very important for their successful applications. The study presents the effect of HPHT conditions on the viscosity of oil-in-water (o/w) emulsions stabilized by nanoparticle-surfactant-polymer for varying concentration of nanoparticle (SiO₂ and clay) in the presence of 1000 ppm polymer (PAM) and 0.22 wt% of surfactant (SDS). The results are compared with the conventional o/w emulsion stabilized by surfactant-polymer system. It is observed that the nanoparticle stabilized Pickering emulsion showed relatively stable viscosity values for varying conditions of pressure and temperature as against the surfactant-polymer stabilized emulsions. The viscosity data for polymer solution is matched satisfactorily with the Carreau model. Herschel–Bulkley model is observed to predict the rheological performance of both o/w emulsion system satisfactorily. The study indicates that the addition of nanoparticle in the surfactant-polymer o/w emulsion system provides noteworthy stability at HPHT conditions, indicating their suitable use for oilfield applications as compared to conventional emulsion.

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