

Investigation of Thixotropy Behavior of Crude Oil—Polyacrylamide Emulsions

Mamdouh T. Ghannam

Department of Chemical and Petroleum Engineering, College of Engineering,
United Arab Emirates University, Al-Ain, United Arab Emirates

Received 12 March 2008; accepted 28 September 2008

DOI 10.1002/app.29586

Published online 23 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This investigation focuses on the study of the thixotropy behavior of crude oil–polyacrylamide emulsions. A wide range of crude oil and polymer concentrations were covered. Crude oil concentrations of 0–75% by volume and polymer concentrations of 0–10⁴ ppm were used. Two polyacrylamides of Alcoflood polymers, AF1235 and AF1285, were examined. RheoStress RS100 rheometer from Haake was employed to study the thixotropy behavior of crude oil–polymer emulsions. Measurements of thixotropy were conducted under the controlled rate mode. The aqueous solutions of Alcoflood polymers show thixotropy behavior. AF1235 aqueous solutions show lower hysteresis rheograms and thixotropy area than the aqueous solutions of AF1285. Polymer concentration

shows strong influence on the ramp-up and ramp-down curves. The crude oil–polymer emulsions behave in an antithixotropy response instead of thixotropy behavior experience for the polymer aqueous solutions. The yield stress values of the crude oil–polymer emulsions increase strongly with polymer concentration for ascending and descending cycles. However, for polymer concentration of less than 1000 ppm, crude oil shows strong effects on the emulsion yield stress values for the ramp-down cycles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 867–875, 2009

Key words: thixotropy; crude oil; polyacrylamide; emulsion; shear stress; shear rate

INTRODUCTION

During the tertiary stage of the crude oil production, polymer aqueous solution is injected into the oil well to enhance the oil production rate. This process leads to the formation of crude oil–polymer emulsion state. Emulsion is the physical status of blending a mixture of two or more immiscible liquids together. The presence of liquid droplets dispersion phase, such as oil, into an immiscible continuous phase of another liquid, such as water, leads to the formation of oil-in-water emulsion (O/W emulsion). Emulsions of different applications are widely available for several technologies. Some examples of these are pharmaceuticals, food, paints, and enhanced oil recovery.¹

The interaction between the oil droplets phase and the aqueous continuous phase is necessary to understand the oil displacement mechanism by the employed polymer solution during the polymer flooding process of the enhanced oil recovery stage. Also, the knowledge of the rheological properties of crude oil–polymer emulsion is necessary for mixing, storage, and pipeline transportation.

The term thixotropy was originally associated with describing isothermal reversible changes of gel–sol, that is, solid–liquid transition, due to mechanical agitation. At present, thixotropy means the continuous decrease of apparent viscosity of high viscous gel status and the subsequent recovery of apparent viscosity of low viscous sol status when the flow is discontinued with time under the effect of shear stress.² Some classes of materials in which thixotropy phenomenon can be encountered are crude oil, greases and waxes, pigment dispersions, food products, polymer solutions, creams, drilling mud, and starch pastes.^{2–4}

The complicated mixture of oil–water emulsion consists of a multi-component and multi-phase system. Numerous articles have investigated the emulsion characteristics from different aspects. Literature survey showed that many studies on the rheological investigation of oil emulsions have been done in which the continuous phase is Newtonian. Some examples of these studies are Sherman,⁵ Princen,^{6,7} Princen and Kiss,⁸ and Pal and Rhodes.⁹ On the other hand, the rheological properties of dispersed solid particles in liquid emulsions have been published in several studies such as Tanaka and White,¹⁰ Chan and Powell,¹¹ Metzner,¹² Gupta and Seshadri,¹³ and Poslinski et al.¹⁴ Limited work has been found on the crude oil emulsion rheological behavior in which the continuous phase is a non-

Correspondence to: M. T. Ghannam (mamdouh.ghannam@uaeu.ac.ae).

Newtonian polymer solution. Some examples of these articles are Han and King,¹⁵ Pal,¹⁶ and Ghannam.¹⁷

For dilute oil phase concentration within the Newtonian continuous phase, viscosity increases linearly with oil concentration. For the medium oil phase concentration, viscosity increases nonlinearly, whereas the emulsion is still Newtonian. However, at high oil phase concentration, emulsions behave in a non-Newtonian pseudoplastic fashion associated with yield stress at an oil concentration higher than 75%.^{6–8} In the rheological behavior investigation of crude oil emulsions in which the continuous phase is Alcoflood polymer (i.e., polyacrylamide) solution, Ghannam¹⁷ reported a non-Newtonian pattern of shear thinning response. The emulsion viscosity enhances with polymer concentration and decreases with shear rate. At a shear rate less than 10 s^{-1} , the type of Alcoflood polymer plays a significant role for the emulsion viscosity. However, for shear rates higher than 10 s^{-1} , the emulsion viscosity shows no significant differences between the different Alcoflood polymer emulsions. Also, the previous investigation of Ghannam¹⁷ reported that the well-known model of Casson,¹⁸ eq. (1), very reasonably fits the flow behavior of crude oil-Alcoflood polymers.

$$\tau = (\tau_0^{0.5} + (\dot{\gamma}\eta_c)^{0.5})^2 \quad (1)$$

where τ is the applied shear stress in Pa, τ_0 is the apparent yield stress parameter determined by Casson model in Pa, $\dot{\gamma}$ is the corresponding shear rate in s^{-1} , and η_c is the Casson apparent viscosity in Pa.s. Casson¹⁸ developed a microrheological model to describe the flow behavior of the structured suspensions. Unlike the Bingham model, eq. (2), the Casson model describes the nonlinearity of plastic behavior.

$$\tau = \tau_0 + \dot{\gamma} \quad (2)$$

Solutions with microstructure usually display thixotropy phenomena, which determine the magnitude of the changes occurring from one state of microstructure to another and back again. The microstructure changes occur by the balance between the breakdown due to flow stress, the buildup due to nonflow collisions and the Brownian motion. All of these activities dictate the level of emulsion viscosity, and all of these activities require time to change from one state to another under the shear applied. When the emulsion molecules and polymer entanglement are randomly distributed, these contributions usually increase the viscosity level and the elastic response. However, when there is uniform distribution of emulsion molecules and polymer alignment in the flow direction under shear, the emulsion viscosity decreases significantly.¹⁹

If a thixotropic structural material is placed in a viscometer, at rest, the microstructure is a combination of large flocs. When the shear rate increases progressively and enough time is allowed, the floc size decreases continuously. At high shear rate, the floc will be disintegrated into its individual constituents. This process of breakdown happens over some time. If the opposite process takes place, that is, the shear rate is instantaneously decreased, the individual constituents start to colloid and flocculate with each other till the size of the floc corresponds to the new status. This process of buildup also happens over time but with a different rate than the breakdown process.¹⁹

Among the recommended methods to measure thixotropy from the flow curve is the hysteresis cycle.²⁰ The hysteresis loop consists of the area enclosed between the up-curve rheogram (i.e., ascending curve for increasing shear rate) and the down-curve rheogram (i.e., descending curve for decreasing shear rate). This area is called the thixotropic area. The opposite phenomenon also exists, and it is known as antithixotropy in which shearing can promote temporary aggregation rather than breakdown due to the collision of the individual constituents particles.¹⁹ For the latter case, the descending curve rheogram will be positioned above the ascending curve rheogram showing negative thixotropic area.²¹

The purpose of this study is to investigate the thixotropy behavior of the crude oil–Alcoflood polymer emulsions. This study examined a wide range of concentration for polymer and crude oil. Two different types of Alcoflood polymers were used in this investigation.

EXPERIMENTAL

A limited work has been published on the rheological investigation of crude oil emulsions in which the continuous phase is a non-Newtonian polymeric solution. The main objective of this work is to study the thixotropic behavior of crude oil–polymer emulsion. Crude oil from Shell Canada Limited was used in all the experimental work of thixotropy investigation. The crude oil density and viscosity are 880.6 kg/m^3 and 7.16 mPa.s at 40°C , respectively. Alcoflood polymer is a high molecular weight polyacrylamide copolymer supplied by Ciba Specialty Chemicals (Bradford, West Yorks, England). Two different types of Alcoflood, AF1235 and AF1285, were used for this study. AF1235 is recommended for low-medium permeability reservoirs; however, AF1285 is utilized for high-permeability reservoirs. Alcoflood materials, white water-soluble, were supplied in a granular powder form. Table I shows polymer specifications for AF1235 and AF1285.²²

TABLE I
Polymer Specifications

	AF1235	AF1285
Bulk density (kg/m ³)	800	800
Viscosity of 0.1% solution at 20°C (mPas)	18	37
pH of 1% solution	7.0	7.0

Crude oil–polymer emulsions were prepared from crude oil, aqueous solution of Alcoflood polymer, and an emulsifying agent. Wide ranges of crude oil and polymer concentrations were used. Crude oil concentrations of 0–75% by volume and polymer concentrations of 0–10⁴ ppm were investigated. An aqueous solution of Alcoflood polymer was prepared first by adding a certain weight of Alcoflood polymer material into 1 L of fresh warm water. Sufficient time was allowed to achieve complete polymer dissolution without external mixing to avoid any mechanical degradation. Then crude oil was gradually added into the prepared aqueous solution of Alcoflood polymer that contained 1% by volume of emulsifying agent to prepare the crude oil-in-polymer emulsion. Triton X-100 was used as an emulsifying agent for the crude oil into the aqueous phase of the Alcoflood polymer. Triton X-100, with a specific gravity of 1.07, is a nonionic surfactant supplied by Sigma-Aldrich Canada. The presence of Triton X-100 within the crude oil–aqueous solution offers two important roles to stabilize the emulsion. The first role is to lower the interfacial tension of the crude oil–aqueous phase, which assists in the formation of the emulsion system. The second role is to stabilize the presence of the oil droplets phase within the aqueous continuous phase to prevent the oil droplets coalescence mechanism.¹

Rheostress RS100 rheometer with cone and plate sensor from Haake was used to study the thixotropy behavior of crude oil–Alcoflood emulsions. All measurements were carried out at a room temperature of 22°C. A water bath was connected to the RS100 system to control the temperature. The sample was placed on the plate for 20 min to rest before shearing. The crude oil–polymer emulsions were sheared by rotating the cone, uniformly accelerating and decelerating to observe the thixotropy behavior. Measurements of thixotropy were conducted under the controlled rate CR-mode. The apparatus was programmed to gradually increase the assigned shear rate from 0.15 to 700 s⁻¹. The stresses and the shear rates of the flow curve were recorded, and the results formed the up-curve. To establish the down-curve cycle, a gradual decrease of the shear rate was assigned from 700–0.15 s⁻¹. The cone angle is 4°, and the cone diameter is 35 mm with a gap equals 0.137 mm at the cone tip. All operation procedures,

measurements, and data analysis were controlled and carried out by the Haake software package.

RESULTS AND DISCUSSION

The thixotropy behavior of a material reflects the time-dependent response due to structure changes at the microscopic and molecular levels. When a thixotropic material is exposed to a constant shear rate, the shear stress responds instantaneously and decreases with time, consequently, viscosity decreases with time. Therefore, the viscosity of a thixotropic material is a strong function of a structure parameter α and shear rate $\dot{\gamma}$ as given in eq. (3). The material structure is considered to be shear-dependent, that is, breaking down under high shear and recovering at low shear or at rest. The changes are governed by a rate equation as described by eq. (4). Equations 3 and 4 provide the thixotropic consideration relationship.

$$\eta = \eta(\dot{\gamma}, \alpha) \quad (3)$$

$$d\alpha/dt = f(\dot{\gamma}, \alpha) \quad (4)$$

For time-independent materials, the down-curve rheogram is identical to the up-curve rheogram; whereas the down-curve rheogram of thixotropic material is different from the up-curve rheogram. For a time-dependent response, the up- and down-curves form a hysteresis loop, which provides an area A . The hysteresis area A , Pa/s, of a material is taken to be a measure of the degree of thixotropy with dimension of energy per unit volume, which reflects the amount of energy/volume required to break down the thixotropic structure.

To ensure a complete destruction of the emulsion structure, an experimental test was carried out consisting of a three-part cycle of an up-curve from 0.15 to 700 s⁻¹, a constant shear rate at 700 s⁻¹, and a down-curve back to 0.15 s⁻¹. The duration of each part was 2 min. To check the reliability of the measurements data, a selected number of experimental tests were repeated three times for the same emulsion. The resulted rheograms coincided on top of each other within acceptance tolerance of about $\pm 2\%$.

Characterization of crude oil droplets

A Zeiss optical microscope was used to observe the state of emulsion and to investigate the distribution and interaction of crude oil droplets within the polymer solution. The computer image analyzer system (CIAS) from Kontron Elektronik, Germany consisted of a high-resolution video camera mounted on an optical polarizing microscope, an image processor, a

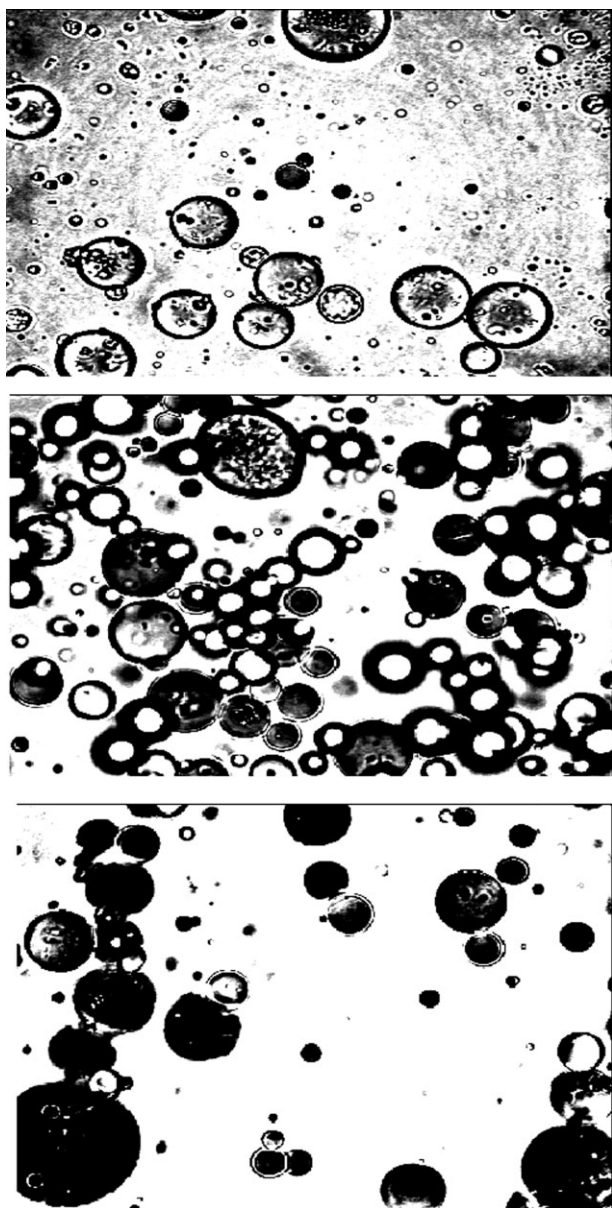


Figure 1 Photomicrographs of crude oil-Alcoflood emulsions. (a) crude oil-water, (b) crude oil-AF1235, and (c) crude oil-AF1285.

Pentium PC, and a high-resolution image monitor. In addition, the CIAS has a powerful facility to enhance the captured image in terms of sharpening, edge detection, threshold function, transition filter, chord sizing, and dilation. Figure 1(a-c) show typical photomicrographs for crude oil emulsions in which water, AF1235, and AF1285 served as a continuous phase, respectively. The crude oil and polymer concentrations are 25% and 1000 ppm, respectively, in these emulsions. It is clear from Figure 1(a) that the crude oil dispersed in the water phase and the oil droplets are almost apart from each other. However, if the Alcoflood polymers are added into the continuous phase, the degree of

aggregation of the crude oil droplets increases in the presence of polymer. At high crude oil concentrations, the crude oil aggregates and forms an interconnected network structure, which will translate to the observed yield stress. The Sauter mean droplet diameter D_{sm} , eq. (5), is employed to measure the mean droplet diameter for these photomicrographs. Where D_i is the droplet diameter and N_i is the number of droplets.

$$D_{sm} = \frac{\sum N_i D_i^3}{\sum N_i D_i^2} \quad (5)$$

The droplet mean diameters are 14, 8.5, and 7 μm , respectively. It is clear that the mean droplet diameters of oil droplets in the presence of polymer are smaller than in water phase.

Thixotropy behavior of polymer aqueous solutions

Figure 2 shows the rheogram behavior for a wide concentration range of AF1235 as a typical example for other aqueous solutions of Alcoflood polymers. This figure displays the ascending curve and the descending curve obtained by applying the shear rate ramp cycle as described earlier. The aqueous solutions of Alcoflood polymers of AF1235 and AF1285 display thixotropic behavior, that is, the up-curves are placed higher than the down-cycle curves. Figure 2 also shows that the polymer concentrations provide a significant influence on the rheograms behavior, that is, the higher concentrations of Alcoflood polymer produce higher cycles of up- and down-curves. The same behavior is reported for the aqueous solutions of AF1285. Figure 3 shows the comparison between the thixotropy behavior for AF1235 and AF1285 at a polymer concentration of 5000 ppm as a typical example for the other examined concentrations. Figure 3 shows that the rheogram hysteresis loop of AF1285 is significantly higher than the AF1235 response. It also displays the destruction of the AF1285 polymer network

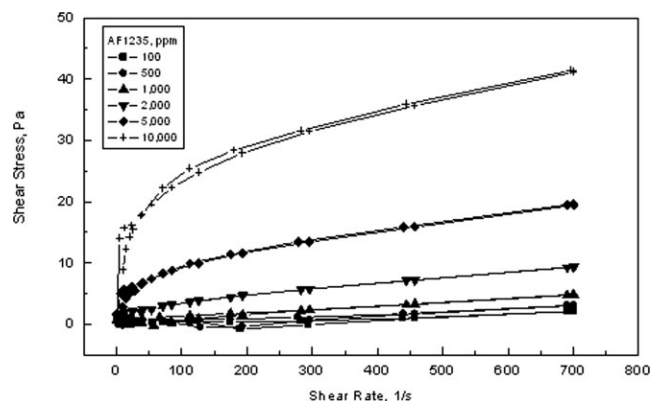


Figure 2 Thixotropy behavior of AF1235 aqueous solutions.

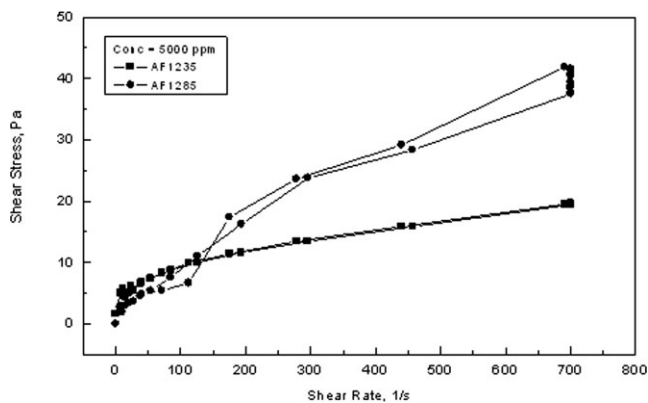


Figure 3 Thixotropy behavior for different Alcoflood polymer solutions.

structure at a constant shear rate of 700 s^{-1} . This behavior was not observed for the AF1235 aqueous solutions as can be noticed from Figure 3. Figure 4 displays the effect of polymer concentration on the area under the up-curve and down-curve for the aqueous solutions of AF1235 and AF1285. For polymer concentration less than 1000 ppm, Figure 4 shows that the area reported for AF1285 is slightly higher than AF1235. This effect is much more pronounced when the polymer concentration increases beyond 1000 ppm. This behavior can be attributed to the viscosity of the AF1285 is higher than AF1235.¹⁷ To anticipate the effect of polymer concentration on the thixotropic area of the Alcoflood aqueous solutions, the modeling analysis was carried out following eq. (6). The regression results for the aqueous solutions of AF1235 and AF1285 are reported in Table II in addition to the regression coefficient r .

$$TA = a \exp(bX) \tag{6}$$

Where TA is the thixotropic area in Pa/s, a and b are the regression coefficients of eq. (6), and X represents the polymer concentration in ppm.

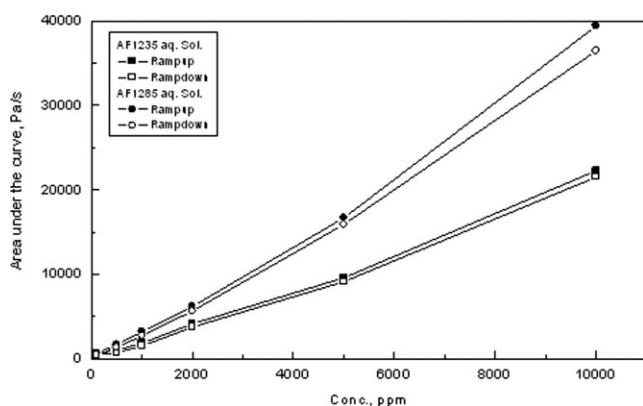


Figure 4 Area under the ramp-up and ramp-down curves for polymer solutions.

The yield stress measurements for polymer aqueous solutions were carried out at a temperature of 22°C using RheoStress RS100 under controlled stress mode. Controlled stress rheometers provide the most direct technique for yield stress measurements. Shear stress in the sample is progressively increased with no shear flow reported till the yield stress is reached. Each test of the yield stress measurements consists of two cycles. In the first cycle, the applied stress was increased gradually over an assigned range to establish the upward curve. Then, the applied stress was instantaneously lowered to obtain the downward curve. In the controlled stress mode, the Haake RS100 applies shear stress using an extremely low inertia. The drive shaft of the RS100 is centered by an air bearing to deliver an almost frictionless applied stress. Therefore, this controlled stress technique makes it possible to measure even extremely small yield stress.

The Casson model is utilized to predict the two parameter coefficients of eq. (1). These parameters are the Casson’s apparent yield stress τ_0 in Pa and the Casson’s apparent viscosity η_c in Pa.s. The apparent yield stress can be considered as the transition limit between two distinct behaviors, which are solid-like behavior and liquid-like behavior. The solution behaves elastically with recoverable deformation below the yield stress. Above the yield stress value, the solution deforms continuously as a viscous liquid without recoverable deformation. Over the polymer concentration range of $100\text{--}10^4$ ppm, Tables III and IV show the Casson modeling analysis parameters for the aqueous solutions of AF1235 and AF1285. These results were obtained for up-curve and down-curve cycles for each solution. Table III shows the results for the aqueous solutions of AF1235. The yield stress value increases slightly with polymer concentration up to 1000 ppm. Above this critical concentration, polymer concentration shows strong effects on the values of yield stress. The downward curve cycle provides lower yield stress values than the upward curve cycle. This means that the AF1235 sample did not fully recover.

Table IV shows the modeling analysis for AF1285 aqueous solutions. Polymer concentration does not show significant effect on the yield stress values up to 2000 ppm. Beyond this concentration, yield stress increases significantly with concentration. At higher concentrations of AF1285, Table IV shows almost no

TABLE II
Thixotropic Area Analysis for Alcoflood Aqueous Solutions

Polymer type	a	b	r
AF1235	272	$1.04 (10)^{-4}$	0.98
AF1285	284.4	$2.331 (10)^{-4}$	0.99

TABLE III
Casson Analysis for AF1235 Alcoflood
Aqueous Solutions

Conc. (ppm)	$\tau_{0 \text{ up}}$	$\eta_{c \text{ up}}$	$\tau_{0 \text{ down}}$	$\eta_{c \text{ down}}$
100	0.218	0.001	0.006	0.003
500	0.269	0.002	0.009	0.004
1000	0.433	0.003	0.014	0.008
2000	1.162	0.006	0.215	0.012
5000	3.576	0.010	3.180	0.011
10^4	10.34	0.021	9.100	0.018

difference between the yield stress values for up-curve and down-curve.

The aqueous solution of Alcoflood polymers displays thixotropy behavior due to the microstructure changes that occurred during the flow process from rest to another state and back again to the rest conditions. The microstructure changes can be attributed to the competition between the breakdown mechanism due to the flow stresses and the buildup mechanism due to the nonflow collisions. At rest, because of a high entanglement polymer density, the aqueous solutions of Alcoflood polymers form a three-dimensional network structure under no shear conditions. This leads to a high value of emulsion viscosity. When the applied shear exceeds the yield stress value, the three-dimensional network structure deforms or even breaks down leading to a lower value of emulsion viscosity.

Thixotropy behavior of crude oil-in-Alcoflood polymer emulsions

To understand the role of crude oil on the thixotropy behavior of the polymer emulsion, it is recommended to investigate the thixotropy profile of the crude oil-in-water emulsion first. Figure 5 shows the ascending curve, descending curve, and the thixotropic area for the crude oil-in-water emulsion over a wide range of oil concentrations of 0–75 vol %. As can be seen from Figure 5 the differences between the ascending and descending cycles decrease with oil concentration, and therefore the thixotropic area slightly decreases with the presence of dispersed oil phase. During the descending cycle, the presence of

TABLE IV
Casson Analysis for AF1285 Alcoflood
Aqueous Solutions

Conc. (ppm)	$\tau_{0 \text{ up}}$	$\eta_{c \text{ up}}$	$\tau_{0 \text{ down}}$	$\eta_{c \text{ down}}$
100	0.228	0.001	0.005	0.003
500	0.165	0.004	0.016	0.007
1000	0.116	0.01	0.07	0.014
2000	0.112	0.02	0.345	0.034
5000	0.747	0.046	0.963	0.045
10^4	5.679	0.08	5.679	0.071

more crude oil phase enhances the regain of the original oil structure phase within the emulsion under the random collisions action of the oil droplets (i.e., Brownian motion) and the shear-induced effect.

Figures 6 and 7 show the thixotropy behavior for crude oil-Alcoflood polymer emulsions. Figure 6(a) shows the ascending and descending cycles for the 5000 ppm of AF1235 for different oil concentrations. Similar behavior is reported for crude oil-AF1285 emulsions in Figure 7(a). As can be concluded from Figure 6(a), the presence of crude oil significantly raises the rheogram response and increases as well the enclosed area between the ascending and descending curves. Figure 6(b) shows that the ascending cycle is placed above the descending cycle for the aqueous solution of AF1235. However, an opposite response is reported for the presence of crude oil within the emulsion with the AF1235 as can be seen in Figure 6(c). The presence of crude oil within the polymer emulsion causes the rheogram behavior to convert from thixotropic profile, in the case of aqueous solutions, to the antithixotropic one, that is, the ascending curve is placed below the descending curve. This type of behavior can be attributed to the effect of two roles. The first role is the Brownian motion and the other is the shear-induced effect. Brownian motion is the random agitation of atoms and molecules resulting from the destruction of the microstructure being sheared. This type of constant random motion allows the atoms and molecules to move to favorable positions to attach themselves to the microstructure.¹⁹ The shear-induced effect allows,²¹ under decreasing shear period of the ramp-down cycle, oil droplets to regain their original shape which enhances the re-structuring process of the oil-Alcoflood polymer emulsions. Similar behavior was reported for crude oil-AF1285 emulsion as in Figure 7(a). Figure 7(b) shows the thixotropy behavior of the AF1285 aqueous solution, whereas Figure

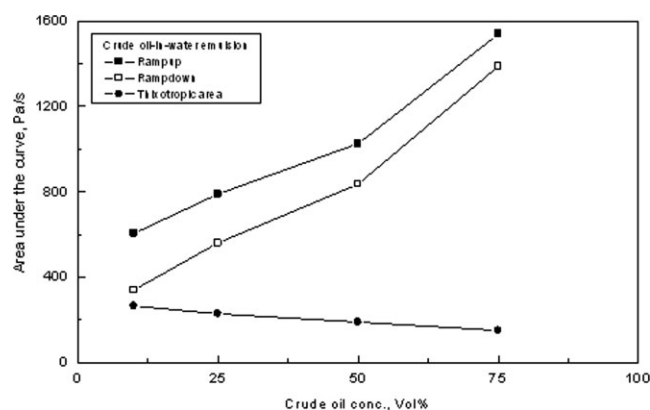


Figure 5 Thixotropic area for crude oil-in-water emulsion.

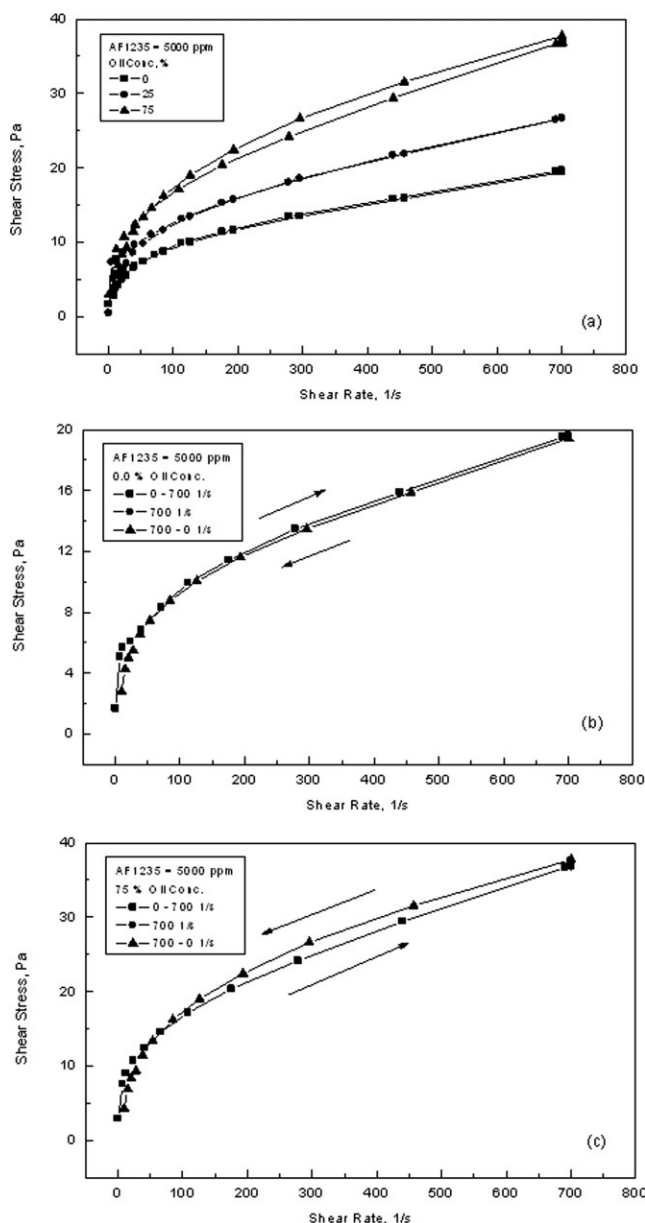


Figure 6 Thixotropic profile for crude oil-AF1235 emulsions.

7(c) shows the antithixotropy profile of the crude oil-AF1285 emulsion. Table V reports all the thixotropic area for the crude oil-Alcoflood polymer emulsions as a function of polymer and crude oil concentrations. The positive and negative values in Table V are for thixotropy and antithixotropy behavior, respectively.

Figures 3 and 7 show a certain degree of cross-overs of the measured data. These can be interpreted as a consequence of the formation and destruction of aggregates. Dupuis et al.²³ studied the shear thickening and time-dependent phenomena of the Polyacrylamide solutions. They concluded that the solution viscosity depends on time and displays a transient regime with strong instabilities. When a polymer emulsion is sheared, the macromolecules

are deformed and directed in the flow. Furthermore, collisions generating from the thermal agitation and shear induced can be the origin of the aggregates formation, which involves frequencies of association and dissociation mechanisms. When a shear stress is applied to an emulsion, the flow is started, viscosity decreased, and the rate of aggregates dissociation is increased while shear rate increased. On the other hand, because of the effect of the thermal agitation and shear induced, the rate of the aggregates association is increased, which increases the emulsion viscosity.

Casson model, eq. (1), is utilized to carryout the modeling analysis for the crude oil-polymer emulsions. This analysis covers a wide range of oil

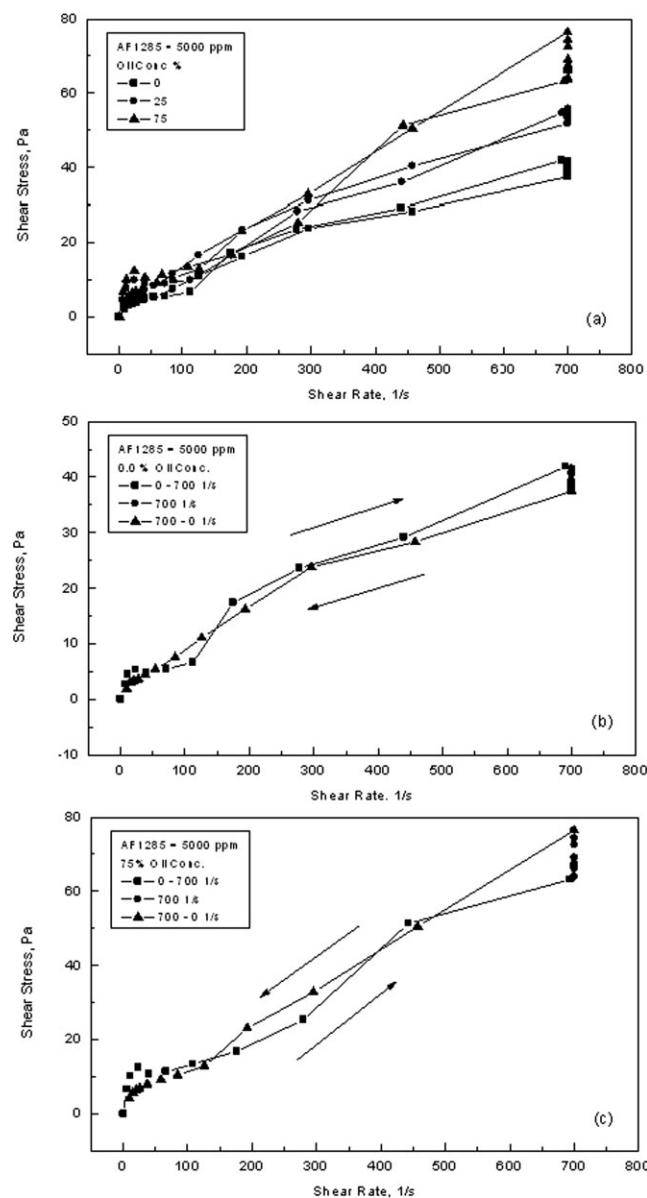


Figure 7 Thixotropic profile for crude oil-AF1285 emulsions.

TABLE V
Thixotropic Area for Crude Oil-Alcoflood Emulsions

Polymer conc. (ppm)	Oil-AF1235 Emulsion		Oil-AF1285 Emulsion	
	25% oil area (Pa/s)	75% oil area (Pa/s)	25% oil area (Pa/s)	75% oil area (Pa/s)
100	219.4	18.3	288.8	-5.0
500	173	-114.8	84.12	-297.4
1000	1.0	-244	-45	-650
2000	-25	-834	-453	-964.1
5000	-70	-1070	-2060	-2120
10 ⁴	-135	-1599	-3550	-4549

concentrations of 0–75 vol % and polymer concentration of 0–10⁴ ppm. The results of this analysis in terms of yield stress are displayed in Figure 8 for AF1235 as a typical example. Figure 8 shows the yield stress values for the ascending and descending cycles for different emulsions. The yield stress values for both cycles increase significantly with polymer concentration. Crude oil shows slight influence on the yield stress values of the ascending cycles. However, it shows a strong effect on the yield values of the descending cycles up to a critical polymer concentration of 10³ ppm. Below 10³ ppm of AF1235 concentration, the yield stress of descending cycles increases significantly with crude oil concentration. Therefore, below a polymer concentration of 10³ ppm, the crude oil concentration plays a significant role to rebuild the emulsion structure. Beyond the critical concentration of 10³ ppm of Alcoflood polymer, the three curves of the descending cycles approach each other and coincide with the ascending cycle values at the polymer concentration of 10⁴ ppm. Above 10³ ppm of AF1235, the role of crude oil gradually diminishes with regards to the role of AF1235 in rebuilding the emulsion structure.

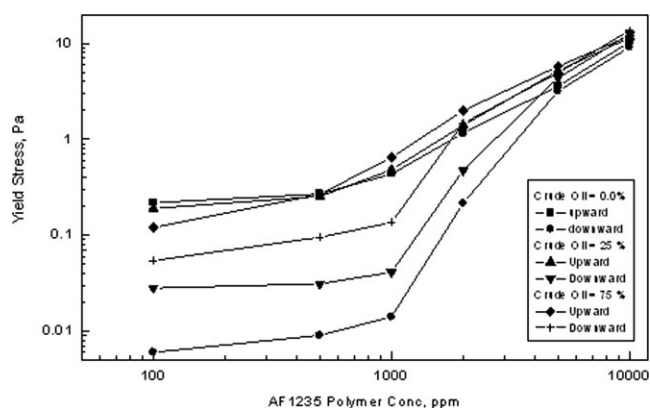


Figure 8 Yield stress behavior of different crude oil-AF1235 emulsions.

CONCLUSIONS

This experimental work was carried out to study the thixotropy behavior of crude oil-Alcoflood polymer emulsions. It is found that the aqueous solutions of Alcoflood polymers display thixotropy behavior. The aqueous solution of AF1285 provides higher hysteresis rheograms and thixotropy area than the aqueous solution of AF1235. The polymer concentration influences the behavior of ascending and descending rheograms. The yield stress for AF1235 aqueous solution increases slightly with polymer concentration up to 1000 ppm. Beyond this concentration, the yield stress increases significantly with polymer concentration. Although, in the case of AF1285 aqueous solution, the yield stress does not change significantly with polymer concentration up to 2000 ppm, for higher polymer concentration of AF1285, the yield stress enhances strongly with polymer concentration. The presence of crude oil phase within the O/W emulsions causes a slight decrease of the thixotropic area. Also, the presence of crude oil phase within the emulsions of both polymers leads to antithixotropic response instead of a thixotropic response in the case of polymer aqueous solutions. The polymer concentration strongly enhances the yield stress values for crude oil-polymer emulsions for ascending and descending cycles. However, the oil concentration causes a slight effect on the emulsion yield stress for ascending cycles. For the descending cycles and polymer concentration below 1000 ppm, emulsion yield stress increases significantly with oil concentration. Above 1000 ppm of polymer concentration, the yield stresses of the descending cycles approach the ascending curves.

References

- Sherman, P. In *Encyclopedia of Emulsion Technology*; Becher, P., Ed.; Marcel Dekker: New York, 1983; Vol. 1.
- Mewis, J. J. *Non-Newtonian Fluid Mech* 1979, 6, 1.
- Scott-Blair, G. W. *A Survey of General and Applied Rheology*; Pitman: London, 1943.

4. Weltmann, R. N. In *Rheology Theory and Applications*; Eirich, F. R., Ed.; Academic Press: New York, 1960; Vol.3.
5. Sherman, P. *Industrial Rheology*; Academic Press: London, 1970.
6. Princen, H. *J Colloid Interface Sci* 1983, 91, 160.
7. Princen, H. *J Colloid Interface Sci* 1985, 105, 150.
8. Princen, H.; Kiss, A. *J Colloid Interface Sci* 1986, 112, 427.
9. Pal, R.; Rhodes, E. *J Rheol* 1989, 33, 1021.
10. Tanaka, H.; White, J. *Polym Eng Sci* 1980, 20, 949.
11. Chan, D.; Powell, R. *J Non-Newtonian Fluid Mech* 1984, 15, 165.
12. Metzner, A. *J Rheol* 1985, 29, 739.
13. Gupta, R.; Seshadri, S. *J Rheol* 1986, 30, 503.
14. Poslinski, A.; Ryan, M.; Gupta, R.; Seshadri, S.; Frechette, F. *J Rheol* 1988, 32, 703.
15. Han, C.; King, R. *J Rheol* 1980, 24, 213.
16. Pal, R. *J Rheol* 1992, 36, 1245.
17. Ghannam, M. *J Chem Eng Jpn* 2003, 36, 35.
18. Casson, N. In *Rheology of Dispersion Systems*; Mill, C., Ed.; Pergamon: New York, 1959.
19. Barnes, H. *J Non-Newtonian Fluid Mech* 1997, 70, 1.
20. Cheng, D. C.; Evans, F. *Br J Appl Phys* 1965, 16, 1599.
21. Kawashima, Y.; Hino, T.; Takeuchi, H.; Niwa, T.; Horibe, K. *Int J Pharm* 1991, 72, 65.
22. Ciba Specialty Chemicals, Private communication, 2001.
23. Dupuis, D.; Lewandowski, F.; Steiert, P.; Wolff, C. *J Non-Newtonian Fluid Mech* 1994, 54, 11.