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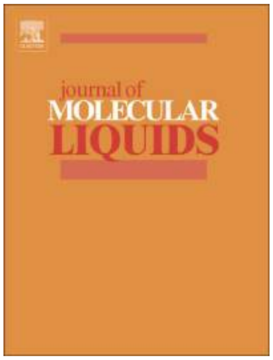

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Review Article

Hydrophobically Associating Polymers for Enhanced Oil Recovery – Part B: A Review of Modelling Approach to Flow in Porous Media.

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Abstract

Polymer flow in porous media represents an entirely different scenario compared to bulk flow analysis using viscometers. This is due to the geometry and configuration of the medium which is made up of converging-diverging flow paths. In this article, a review of the single-phase flow of hydrophobically associating polymers in porous media is presented. Hydrophobic association between these polymer chains have been reported to occur and vary under reservoir conditions (temperature, salinity, and ion concentration). However, under these conditions, the critical aggregation concentration of associating polymers have been observed to change and the extent of change is a function of the hydrophobe make-up of the polymer. The outcome of this would indicate that polymer injectivity and its oil recovery efficiency are affected. As such, an understanding of the mechanism, propagation and sustainability of these hydrophobic interactions in reservoirs remains a critical focus of research. This becomes even imperative as the in-situ rheological profile associated with the different flow regimes may be affected. A numerical approach to investigating the real-time hydrophobic interactions between associating polymer chains during flow in porous media remains the viable option. However, this would require modifying existing time-independent models to accurately predict the various flow regimes and the dispersion of associating polymers to account for hydrophobic interactions.

Keywords: Enhanced Oil Recovery; Associating Polymers; Porous Media; Hydrophobic Interactions.

1. Introduction

The critical aggregation concentration (CAC) of hydrophobically associating polymers (HAPAM) is the threshold concentration that characterizes its rheological behaviour (Figure 1). Below the CAC, intramolecular interaction within the polymer chain dominates the rheology (Taylor and Nasr El-Din, 1998; Yabin et al., 2001; Feng et al., 2005; Lu et al., 2010; Afolabi, 2015; Akbulut and Temizel, 2017; Afolabi et al., 2019). Under these conditions, hydrodynamic volume is low with no network formation between polymer chains resulting in low polymer viscosity (Taylor and Nasr El-Din, 1998; Yabin et al., 2001; Zeynali et al., 2004; Taghizadeh and Foroutan, 2005; Romero, 2009; Alquraishi and Alsewailem, 2012; Gou et al., 2015; El-Hoshoudy et al., 2017; Bai et al., 2018). This particular phase is described as the “dilute region”. Beyond the CAC, intermolecular association arising from hydrophobic interactions between polymer chains dominates the rheological behaviour of aqueous solutions formulated from HAPAM (Gou et al., 2015; Sun et al., 2015; Chen, 2016; Bai et al., 2018). This brings about a network of molecular association between the polymer chains, which in turn increase the hydrodynamic volume and viscosity. This phase beyond the CAC is described as the “semi-dilute region” (Feng et al., 2005; Zhao et al., 2009; Jiang et al., 2013; Lai et al., 2013; Sun et al., 2015; El-Hoshoudy et al., 2017; Gong et al., 2017; Bai et al., 2018). At higher concentrations, there is the “concentrated region” however, there is not much of a distinction from the semi-dilute regime. As mentioned earlier, the outcome of these attributes of HAPAM polymers above the CAC is high mobility control, improved thermal and salinity tolerance and an overall improved EOR performance in comparison to hydrolysed polyacrylamide (HPAM) (Yabin et al., 2001; Zeynali et al., 2004; Feng et al., 2005; Taghizadeh and Foroutan, 2005; Zhao et al., 2009; Lai et al., 2013; Sun et al., 2015; El-Hoshoudy et al., 2017; Bai et al., 2018). Apparently, this common understanding about the CAC is evident from bulk rheological characterization which is the focus of numerous scientific publications on HAPAM over the last decade. However, flow in rheometers or viscometers represents a different geometrical configuration to a porous media. The flow of polymers in a porous media can be attributed to the existence of both shear and extensional components (Sochi, 2010; Stavland et al., 2010; Zamani et al., 2015; Lohne et al., 2017; Zamani, et al., 2017; Skauge et al., 2018). In differentiating between these components, Figure 2 shows a fluid element (A) subjected to both shear and extensional flow. Under shear flow, the distance between points on any streamline is the same. However, under extensional flow, the horizontal distance between points on the same streamline changes and appears stretched while streamlines appears closer. In other words, if the time period between points is such that polymer molecules can return to their equilibrium state after shear deformation, then there would be no extensional viscosity. However, the contraction allows closer contact between streamlines enabling interaction between them which in the case of HAPAM promotes increased associative interactions. In addition, if the time between contractions is less for the polymer molecules to return to its equilibrium state, they would remain stretched and extensional viscosity is observed. Therefore, a fluid element is in extensional or elongational flow when it is subjected to extensions or compressions which dominates over shear effects. In like manner, Skauge et al. (2018) used the coil-stretch model to explain the phenomenon of polymer extensional flow. Polymer molecules can be visualized as entangled coils and when subjected to flow, two competing forces arise. Firstly, there is a force (entropic force) which tries to maintain the existing polymer configuration and the magnitude of this force is a function of the degree of polymer entanglement. For HAPAM, this is dependent on the magnitude or strength of the hydrophobic interactions. Secondly, a drag force comes into play arising from the interaction between polymer molecules and the solvent in which it is dissolved. When the drag force is below the entropic force, the polymer molecules take up a coiled configuration and the viscosity is maintained. However, when the drag force exceeds the entropic force, polymer molecules become disentangled and align in the flow direction. Under these conditions, polymer viscosity reduces and shear thinning sets in (Taylor and Nasr El-Din, 1998; Feng et al., 2005; Kamal et al., 2015; Wang et al., 2018; Li et al., 2018). At the point where these molecules are completely aligned to the flow direction, they would start to stretch at increasing flow rates and shear thickening (or extensional viscosity) sets in. For such polymer flow in porous media, the extensional component is related to the converging-diverging flow channels. Furthermore, polymer flow in a porous media with low tortuosity and aspect ratio (i.e. contrast between pore body and pore throat) would have a viscosity profile similar to what is obtainable in bulk viscosity. This is due to the less exposure of the polymer molecules to extensional fields and as such the shear rate calculation may focus on the shear terms with the extensional components negligible. Overall, shear thickening of polymers can be described as an irreversible increase in viscosity which can eventually lead to polymer degradation. However, the associative interaction between HAPAM polymers can be described as a reversible thickening effect which can be characterized by a transition between intramolecular and intermolecular associations (Guo et al., 2016). This transition point between intramolecular and intermolecular associations can be monitored by an understanding of the uncertainty in the molecular weight and eventual effects of polydispersivity of HAPAM polymers. As such, a change in CAC can be identified to mark transition between the two forms of molecular association. This would enable proper evaluation of the sustainability and propagation of hydrophobic interactions in a porous media under dynamic conditions. In addition, this would depend on the extent to which the CAC of the polymers is affected by the conditions of the reservoir. In other words, the long-term stability of these hydrophobic interactions would depend on finding the right balance between the CAC and oilfield conditions (rock adsorption, temperature, salinity, shear and pH). More so, modelling the degree of hydrophobic interactions between associating polymers in porous media will be vital towards highly reliable design, computational modelling and preparation of economical flooding operations. Existing viscosity models for describing flow behaviour of aqueous polymer solutions in porous media have been applied to HAPAM with particular emphasis on shear thinning without a detailed focus on extensional flow. Similarly, predictive modelling of the flow of associating polymers in porous media would constitute a different perspective. This is as a result of the different trends to hydrophobic interactions between polymer chains under static and dynamic conditions. For example, the molecular weight distribution of associating polymers would differ before the flow, during flow and after flow in a porous media. This would also mean that the degree of hydrophobic interactions would differ in the three cases mentioned. Therefore, accurate prediction of in-situ rheology would require capturing the impact of hydrophobic interaction associated with these polymers during flow in a porous media. More so, the reuse of these polymers requires a comparison between its pre-flooding and post-flooding solution properties. As such, proper characterization of produced fluid containing associating polymers would indicate the likely reuse of these polymers. This would ensure cost saving on finding an environmentally friendly disposal approach to a produced fluid containing such polymers. Therefore, this review looks at the available background to the flow of hydrophobically associating polymers in porous media and integrates it in a wider theoretical framework. This theoretical framework looks at relating critical properties (CAC and Critical Shear Rate) of HAPAM polymers to oil field parameters. This was done to incorporate new discoveries and find plausible explanations based on existing scientific knowledge. However, where this does not provide reasonable explanations, a rationale was provided for future research which include developing novel modelling approach. Consequently, the discussions which underpin this review are based on the following questions:

a) Can the hydrophobic association between HAPAM polymers be continuously sustained in a porous media?
b) Are existing predictive models, in their present form, sufficient to describe the flow behaviour of associating polymers in porous media?
c) Where a change in CAC occurs within the conditions of a reservoir, will the thickening property of the produced HAPAM polymers be significantly affected?

2. The Flow of Hydrophobically Associating Polymers in Porous Media

The flow behaviour of HAPAM polymers investigated with the use of viscometers and rheometers has been reported in literature (Huaiping et al., 2008; Chen et al., 2012; Deen 2012; Guo et al., 2012; Deng et al., 2014; Li et al., 2017; Khromiak et al., 2018). The property of interest is the bulk polymer viscosity which is measured under steady-state conditions (Ponjavic et al., 2015). A rheological study of HAPAM polymers has attributed its unique features to associative effect at concentrations above the CAC. However, the flow of associating polymers measured with viscometers/rheometers differs significantly from what is experienced in a porous media. According to Skauge et al. (2018), the rheology of polymers as measured with these instruments differs from what is obtained in a porous media; the reasons for this include the following:

a) The geometry of porous media is inherently complex compared to viscometers or rheometers.
b) The flow behaviour in viscometers or rheometers is essentially shear thinning whereas polymers are viscoelastic with a tendency for shear thickening above a critical shear rate.
c) Polymer exposure to varied shear rates arising from the presence of numerous expansion-contraction channels.
d) The adsorption and mechanical entrapment of polymer molecules tend to make the geometry of the porous media variable (Garrocuh and Gharbi, 2006).

2.1. In-Situ Rheology of Associative Polymers

To properly account for polymer rheology, the concept of in-situ viscosity has been coined to describe flow behaviour in porous media in comparison to bulk viscosity. In-situ viscosity of a polymer can be defined as the average viscosity inside a porous media and is also described as the apparent viscosity. This differs from the effective viscosity which can be related to the viscosity of the polymer in a pore throat. Figure 3 shows a typical flow curve for a polymer solution in a porous media displaying viscoelastic behaviour at steady-state. Similar trends in porous media have been reported (Edwards et al., 2002; Jiang et al., 2003; Khamees and Flori, 2018). The identifiable flow regimes in a porous media can be classified as Newtonian, Shear Thinning, Shear Thickening and Mechanical Degradation (Hatzignatiou et al., 2013). The Newtonian regime is apparent at low shear rates but beyond initial critical rate γ_{o}, shear thinning is apparent until polymer viscosity reaches a local minimum at a critical shear rate value of γ_{c}. This critical shear rate, which is one out of three, represents the threshold for the onset of shear thickening. A local maximum for the polymer viscosity is obtained at a third critical rate γ_{m}. Beyond γ_{m}, there is another decrease in polymer viscosity; this shear rate is characterized as the onset of mechanical degradation (Dupas et al., 2012; Brakstad and Rosenkilde, 2016; Lohne et al., 2017; Skauge et al., 2018). Polymer injectivity in porous media is influenced by a number of factors including shear thickening. Injection rates above the critical rate for the onset of shear thickening may reduce polymer injectivity for field application (Skauge et al., 2018). At this point, polymers undergo an irreversible thickening effect which culminates into degradation after a given period. The critical shear rate for the onset of dilatant behaviour in porous media depends on polymer, solvent and rock properties. However, in the case of associative polymers, some of the concerns according to Seright et al. (2011) are related to:

a) Maintaining the enhanced viscous properties (long-term stability) and ensuring its propagation in porous media under varied reservoir conditions.

b) The effect of polymer concentration regime on polymer injectivity. An understanding of its effect on the onset of shear thickening in porous media.

As mentioned in (b), the effect of concentration regime of associative polymer flow on the onset of shear thickening is limitedly understood. However, this can be complicated given that certain oil field parameters such as temperature and salinity have been reported to alter the CAC of associating polymers (Zou et al., 2013; Gou et al., 2015; Sun et al., 2015; Quan et al., 2016). In the case of thermal effects, the outcome on the CAC of associating polymers can be described in two ways:

a) For a given degree of hydrophobicity, an increase in temperature would bring about a reduction in polymer viscosity, η. This would imply an increase in the critical aggregation concentration, C_c. What this simply means is that a higher polymer concentration would be required to sustain the associative effect of the hydrophobic groups present in the polymer backbone.

b) Where the degree of hydrophobicity is increased, the energy barrier/activation energy is increased likewise the intrinsic viscosity. As such, the critical aggregation concentration would decrease. However, polymers with a high degree of hydrophobicity would experience a larger drop in viscosity with temperature.

The case of the salinity effect on the CAC of hydrophobically associating polymers was studied by Rashidi et al. (2010). The CAC of the polymers were observed to increase with the degree of salinity. As such, a higher threshold value of CAC would be required for a meaningful hydrophobic associative effect to take place. To express this, a mathematical relationship by Hayahara & Takao (1968) can be used as shown in Equation (1):

$$V_m = \frac{M_w}{C_c N_a} \quad (1)$$

An increase in the CAC, (denoted by C_c), would bring about a decrease in the volume available per polymer chain, V_m. When V_m is reduced polymer chains come together and the hydrophobic associative effect is enhanced. The increment in CAC can be ascribed to an increase in charge density on the polymer chain which decreases polymer hydrodynamic volume. In addition, the incremental effect of salinity on CAC was also validated by the work of Saeed et al. (2017). However, the implication of this on EOR operations would mean:

a) High polymer concentration would be needed, if not above the limit for EOR operations, and this could be detrimental to the economics of the flooding process;
b) Also, polymer injectivity would be affected and this is often constrained by formation fracture pressure.

Ultimately, a salt-tolerant HAPAM polymer is one whose thickening properties are enhanced under increasing salinity. Additionally, rock permeability plays a role in the viscosity profile of polymers in porous media (Clarke et al., 2016). This, in turn, may influence the onset of hydrophobic interaction and that of shear thickening behaviour. Accordingly, Skauge et al. (2018) identified the following possibilities for associative polymers in porous media at a concentration above the CAC:

a) The extent of shear thinning may increase and consequently, the onset and extent of shear thickening may be delayed.
b) The rheological behaviour may change above critical shear rates, γ_c and γ_m, for different polymer concentration regime.

2.2. Mechanism of Associative Polymers Effects on Oil Recovery

Improved oil recovery from the use of polymers has been thought to only recover “bypassed oil” whilst leaving behind a significant residual oil in porous media (Clarke et al., 2015).

Recently, it has been shown that for viscoelastic polymers, there is a transition from steady laminar flow to a strongly fluctuating flow consistent with elastic turbulence (Clarke et al., 2015; Cui et al., 2016). The onset of this elastic turbulence (or flow fluctuations) has been identified as the mechanism behind the additional mobilization of trapped oil (capillary desaturation through destabilization of trapped oil). At flow rate greater than the onset for shear thickening, extensional viscosity cannot be taken as the reason for additional oil recovery when the capillary number (Ca) is less than the threshold ($\mathrm{Ca} \leq 1$). Thus, the degree of trapped oil mobilization is a function of the extent of elastic turbulence generated. However, experimental core flooding using associating polymers for EOR have attributed the improved recovery to the associative interactions. As stated at the beginning of this section, a porous media represents a completely different and complex structural geometry. An interesting phenomenon which has not been mentioned in the literature is the dependency of elastic turbulence on the intermolecular association (hydrophobic interaction) for flow in porous media. This can be manifested in a number of ways depending on the concentration regime of the associating polymer. Firstly, this can take place in the form of multiple shear-thinning regions (or an extensive shear thinning region) if associative hydrophobic interactions occur before the onset of shear thickening. Secondly, this can take place through alteration of the critical shear rate for the onset of shear thickening in porous media. For studies on polyacrylamide/hydrolysed polyacrylamide polymers, it has been reported that it is unusual for polymer solutions to exhibit multiple and distinct shear thinning regions (Tam et al., 1998). Nonetheless, studies on HPAM polymers have indicated divergent views on the influence of polymer concentration on the onset of shear thickening. According to Jiang et al. (2003), for all molecular weights of HPAM polymers, the critical shear rate decreases with increasing polymer concentration. In contrast, Lewandowska (2007) showed that the critical shear rate for the onset of dilatant behaviour in HPAM polymers increases with increasing polymer concentration. The experimental results obtained by Jiang et al. (2003) and Lewandowska (2007) were based on viscometric analysis of HPAM polymers and not flow in porous media. Recently, Clarke et al. (2015) and Clarke et al. (2016), claimed the onset of dilatant behaviour or shear thickening for a HPAM polymer in a porous media is independent of concentration. However, bulk rheological studies on the shear degradation of hydrophobically associating polymers have indicated the ability of these polymers towards improved rheological stability with increased shear rates (Zhuang et al., 2001; Dai et al., 2008; Lai et al., 2013; Sun et al., 2015; Bai et al., 2018). Two possible trends can be deduced from the viscosity profile of associating polymers with an increase in shear rates. Firstly, at a low value of shear rates, there is a rapid decrease in polymer viscosity. Secondly, beyond a particular shear rate, there is a significant decrease in the decline of polymer viscosity (Zhuang et al., 2001; Dai et al., 2008; Lai et al., 2013; Sun et al., 2015; Bai et al., 2018). A logical explanation could be the exposure of the hydrophobic regions of the associating polymer which allow for interaction with increasing shear rates. The initial decrease would coincide with the orientation of the polymer chain in the direction of shear flow. However, translating this explanation to a porous media would mean that intramolecular molecular interactions could transit to intermolecular interactions. Recently, Guo et al. (2016) showed this possibility by conducting core flooding through three serially mounted cores with very similar rock properties (permeability and porosity). It was observed that for associative polymers namely HNT-3.28 and HNT-4.32 (containing 3.28 and 4.32 mol % hydrophobic monomer respectively), the resistance factors (RF) of the polymers were much greater in the second and third cores compared to the first core. Plausible explanation given by the authors was the conversion of intramolecular interactions to intermolecular interactions due to elongational or extensional flow in the porous media. However, this transition between the two interactions depends on the hydrophobic monomer content. Following from the work of

Guo et al. (2016), it was observed that similar trend was not observed with associative polymers HNT-1.1 and HNT-2.2 (containing 1.1 and 2.2 mol % hydrophobic monomer) respectively. It was put forward by the authors that this may be due to low intramolecular interactions such that any transition to intermolecular interaction has been counteracted by polymer-rock interaction such as adsorption. In addition, a distinction should be made between this transition and shear thickening. An explanation is that shear thickening is an irreversible increase in viscosity due to polymer elongation or stretching. However, the transition between these interactions can be viewed as a reversible thickening of polymer viscosity. Therefore, it is obvious that the complex solution properties of associating polymers compared to HPAM in porous media presents a challenge in designing a suitable associating polymers for a particular reservior (Guo et al., 2012; Guo et al., 2016). In general, designing a hydrophobically associating polymer for EOR is hinged on understanding the tolerance of the polymers to oil field parameters and an in-depth understanding of the transition of intramolecular interaction to intermolecular interaction and optimizing for it for improved polymer injectivity.

2.3. Performance of Associative Polymers under Alkali/Surfactant Flooding

The use of HAPAM polymers for Alkaline Surfactant Polymer (ASP) flooding is not common compared to the use of HPAM polymers (Feng et al., 2013; Guo et al, 2017). Feng et al. (2013) compared the use of HAPAM to HPAM polymers in an ASP flooding project in a Daqing class II reservoir (100 – 300 $x10^{-3}\mu m^2$) containing heavy alkyl benzene sulfonate. The authors evaluated the HAPAM polymer under laboratory and field conditions. Figures 4(a) and (b) show the effect of the ASP system containing HAPAM and HPAM on the interfacial tension under laboratory conditions respectively. For the associative polymer in Figure 4(a), it shows good compatibility with heavy alkyl benzene sulfonate, which can ensure very low interfacial tension over a wide range of alkali/surfactant concentration. When aged for a period of 120 days, the viscosity of the associative polymer is improved however, the interfacial tension remained the same. Flooding experiment was conducted using 1000 mg/L HAPAM-ASP system containing 1. % NaOH and 0.3 % alkyl benzene sulfonate. Figure 5 show that using 0.3 PV of ASP fluid improved the recovery of oil by 26 %. The mechanism by which ASP system containing associative polymers improve oil recovery is summarized in Figures 6 and 7. In the presence of the base and the surfactant, the viscosity of the ASP fluid is increased due to higher hydration degree of the carboxylic groups under basic conditions. This ensures that the carboxylic groups on the hydrophilic main chain on the associative polymer are completely dissociated thereby enabling polymer chain extension. Therefore, the surfactants present in the ASP system interacts with the hydrophobic components of the associative polymer thereby resulting in more intermolecular association, which significantly increases the viscosity of the fluid as shown in Figure 7. However, it should be noted the rheological improvement of ASP system containing associative polymers depend on type and composition of the surfactant (Feng et al., 2013). In addition, the composition and type of hydrophobic monomer in the associative polymer is also important when considering the performance of HAPAM-ASP system.

3. Modelling the Flow of Associating Polymers

3.1. Existing Models for In-Situ Polymer Rheology

Due to the time-consuming nature of in-situ measurement techniques, in-situ polymer rheology has often been evaluated analytically and numerically (Skauge et al., 2018). The difficulty with modelling polymer rheology lies in the fact that they are non-Newtonian fluids and the porous media in which they flow is a non-uniform pore geometry (Lohne et al., 2017; Skauge et al., 2018). The analytical study of polymer flow in porous media involves the use of time-independent models with the addition of some viscoelastic attributes (Delshad et al., 2008; Sochi, 2010; Hatzignatiou et al., 2013; Yang et al., 2015). This can be represented as shown in equation (2):

$$\mu_{app} = \mu_{sh} + \mu_{el} \tag{2}$$

Where μ_{sh} represents the shear-thinning component. Modelling the shear thinning features of polymer flow has been captured using the Power law or Carreau model (Skauge et al., 2018). μ_{el} represents the elongational or extensional viscosity attributed to shear-thickening. In another approach, the flow of polymer in porous media is represented as the product of the shear and elastic components as shown in equation (3) (Lohne et al., 2017):

$$\mu_{app} = \mu_{sh}(\mu_{el}) \tag{3}$$

However, regardless of the approach employed (either equation (2) or (3)), a general classification of viscosity models for polymer flow in porous media was grouped into two by Yang et al. (2015). This classification was based on the number of parameters contained in the model: two parameter and multi-parameter models. The only known two-parameter model describing polymer flow in porous media takes the form of the power law model in describing shear-thinning and shear-thickening as shown below in equation (4):

$$\mu_{app}(\gamma) = \begin{cases} K_1(\gamma)^{n_1-1}, \ \gamma < \gamma_c, \ n_1 < 1 \\ K_2(\gamma)^{n_2-1}, \ \gamma > \gamma_c, \ n_2 > 1 \end{cases} \tag{4}$$

Where K_1, K_2, n_1, and n_2 are the consistency and flow index parameters representing the model. These parameters are similar to what is obtainable in the power law viscosity model. The model is simplistic in form and its application is limited due to lack of clarity in differentiating between the shear thinning and shear thickening stage (Yang et al., 2015). In other words, accurate prediction of the onset of shear thickening is not captured by the model. The multi-parameter models take into account variations of polymer viscosity at relatively large shear rates. Table 1 presents known models that make up the shear thinning and shear thickening components of various multi-parameter models used in describing polymer flow in porous media. The multi-parameter models generally give a full description of polymer flow from shear thinning to shear thickening and even polymer degradation. However, the large number of model parameters can be challenging and it may be difficult to estimate them. In like manner, Lohne et al. (2017) described a similar challenge with such models when applied for polymer flow in porous media. In their analogy, the manual tuning of each parameter for proper flow description can be challenging and time-consuming for simulation purposes. However, existence of large number of parameters tend to better quantify the uncertainties surrounding polymer flow in porous media. For associating polymers, the contributions of the hydrophobic interactions to the apparent polymer rheology must be described with sufficient parameters in the model. In addition, variation in oil field parameters (porosity, permeability, temperature, salinity and ion concentration) alter polymer rheology and need to be captured in analytical models. For example, temperature conditions within a reservoir are usually much higher than the injected polymer solution; likewise, the ion concentration of the injected solution is much lower than what is obtainable in the reservoir. These variations as earlier mentioned would alter the solution properties (especially the CAC) of hydrophobically associating polymers and must be captured in the models. Furthermore, the elastic contributions of hydrophobically associating polymers to flow resistance are more significant compared to hydrolysed polyacrylamide. Therefore, it becomes imperative to have a suitable model for predicting the onset of mechanical degradation since polymer mechanical degradation takes place after shear thickening, however, the time scale for the onset of mechanical degradation depends on the elastic contribution of the polymer. Apparently, the subject of polymer mechanical degradation is significant in relation to injection facilities where polymer solutions are exposed to high flow rates and possibly to turbulent conditions. Moreover, the extent of degradation is not only a function of the polymer architecture but also reservoir properties around the well region. In minimizing the number of parameters associated with a model, Lohne et al. (2017) suggested that the time constants defining the transition between flow regimes be expressed as a function of polymer and reservoir properties. As such, the time constants of an appropriate model should capture the effect of concentration regime of associating polymers (dilute and semi-dilute) and the effect of varying molecular weight (hydrophobic character) in addition to the rock properties. The advantage of this approach is that the number of parameters associated with a rheological model would be greatly reduced while allowing for easier regression of experimental results.

3.2. Predicting CAC of Associating Polymers and Correlation to Oil Field Parameters

The Huggins equation is employed for dilute polymer concentrations in the estimation of the intrinsic viscosity $[\mu]$ and this is related to the polymer concentration c in equation (5)

$$\mu_0 = \mu_s + \mu_s(k_0[\mu]c + k_1[\mu]^2c^2) \tag{5}$$

Where k_0 is equal to one, μ_s is the solvent viscosity and k_1 is the Huggins constant. Estimating a value for the CAC of associating polymers involves fitting the Huggins equation to rheological data for dilute polymer concentration. However, a predictive approach for estimating the CAC of associating polymers remains absent. The terms $k_0[\mu]c$ and $k_1[\mu]^2c^2$ characterizes the dispersity of polymer chains with varying length in solution. Predicting the onset of associative interaction between polymer chains can be considered as the concentration at which a single polymer chain interacts with another. This can be predicted by equating the terms $k_0[\mu]c$ and $k_1[\mu]^2c^2$ respectively as shown below in (6)

$$k_0[\mu]c_c = k_1[\mu]^2c_c^2 \tag{6}$$

The critical aggregation concentration, c_c can be simplified from (6) as shown in (7) and (8) respectively

$$c_c = \frac{k_0}{k_1[\mu]} \tag{7}$$

$$c_c = \frac{1}{k_1[\mu]} \tag{8}$$

The critical aggregation concentration can be said to be inversely proportional to the intrinsic viscosity of the polymer. The impact of oil field parameters (such as temperature, salinity, pH and ion concentration) on the CAC of hydrophobically associating polymers has been comprehensively reported (Wyatt et al., 2011; Chen et al., 2012; Zhong et al., 2014; Kamal et al., 2015; Gou et al., 2015; Quan et al., 2016). However, the susceptibility of CAC to changing oil field parameters would have implications on the polymer injectivity and overall economics of the EOR operations. Also, the extent to which the CAC of associating polymers become vulnerable to oil field parameters is a function of the type and quantity of hydrophobic comonomer employed in the polymer synthesis. More importantly, there exists no independent model which correlates the CAC to the various oil field parameters. The use of existing viscosity models (such as Power Law, Carreau, Ellis and Cross) would only relate the model parameters to the CAC or oil field parameters. Therefore, using a specific generic rheological model in its present form would allow for a parameterization of the effect of oilfield parameters on the CAC of associating polymers. However, the aim is to relate the CAC to the influence of the oil field parameters directly. Therefore, further research is necessary to accurately correlate the CAC of associating polymers to oil field parameters. In order to achieve this, a prediction methodology can be developed using multivariate regression analysis as shown in equation (9). A key advantage of this approach is that the CAC is directly related to the oilfield parameters and the model constants arising from it are a function of the type and quantity of polymer used. The significance of this outcome is that the impact of oilfield parameters on the CAC can be directly inferred.

$$y(x_1, x_2, \ldots x_n) = f(x_1, x_2, \ldots x_n) \tag{9}$$

Where y is the CAC of the polymer, $x_1, x_2, \dots x_n$ represents the various field parameters associated with an oil reservoir. For example, considering the field parameters Temperature, T, and Salinity and Hardness, C_s, the CAC values can be made relative to a particular CAC measured for aqueous polymer solution at a given temperature, T_o, in equation (10):

$$CAC_{T,C_s} = k_m CAC_{T_o} \qquad (10)$$

Where CAC_{T,C_s} is the CAC at varied temperature, T and salinity conditions, C_s. k_m is the model coefficient which can be described as the ratio of CAC_{T,C_s} to CAC_{T_o}. Based on the obtained experimental data, the dependency of the dimensionless coefficient, k_m, on temperature and salinity can be estimated. Therefore, equation (10) can be expressed as (11):

$$CAC_{T,C_s} = k_m CAC_{T_o} = f(\Delta T, \Delta C_s) CAC_{T_o} \qquad (11)$$

Where $k_m = f(\Delta T, \Delta C_s)$, ΔT is the temperature difference and ΔC_s is the difference in the salinity concentration. Equation (11) represents a simple function for calculating the CAC at any temperature and salinity conditions. An accurate form of $f(\Delta T, \Delta C_s)$ is vital for the prediction of CAC of associating polymers under varied temperature and salinity conditions. Therefore, the temperature and salinity influence on CAC would have to be analysed separately based on the experimental results and a concrete form for $f(\Delta T, \Delta C_s)$ can be established. The model parameters that would arise from accurately determining the form for $f(\Delta T, \Delta C_s)$ would be dependent on the type of associating polymer and its response to temperature and salinity conditions.

3.3. Predicting Hydrophobic Interactions in Porous Media

The flow of associative polymers in a porous media goes through various regimes as stated earlier. The shear thinning and thickening regimes remains common for viscoelastic polymer studies. Predicting variation in hydrophobic interactions in porous media would require and understanding of the changing polydispersivity of the associative polymers during shear thinning and thickening respectively. According to Lohne, et al. (2017), the polymer relaxation, λ_1 time can be related to both polymer properties (molecular weight, M_w, polymer concentration, c_p and specific viscosity, μ_{sp}) and reservior conditions (temperature, T and salinity by modifying the slovent viscosity, μ_s) as shown in equation (12)

$$\lambda_1 = \left(\frac{6}{5R_g}\right)\left(\frac{\mu_s\mu_{sp}M_w}{c_pT}\right) \tag{12}$$

The authors represented $\left(\frac{6}{5R_g}\right)$ as a tuning parameter, λ_a to account for the effects of polydispersivity of polymer chains in solution. Equation (12) becomes (13)

$$\lambda_1 = \lambda_a\left(\frac{\mu_s\mu_{sp}M_w}{c_pT}\right) \tag{13}$$

Most shear thinning models (Carreau and Cross) have a time constant which can be related based on (13) to estimate the tuning parameter, λ_a. The increase or decrease in the value of λ_a simple reflects the changes in intermolecular interaction under the reservoir conditions of salinity and temperature. Also, a change in the polymer properties such as molecular weight or concentration would affect the tuning parameter as well and as such the hydrophobic interactions. However, porous media effect on hydrophobic interactions needs to be captured and this come into play when considering shear thickening. Important parameters under this flow regime is the onset of shear thickening and the stretch rate. The onset of shear thickening can be estimated by considering the pore residence time and the polymer elongational time. According to Lohne et al. (2017), computation of the pore residence time can be made based on the assumption that the pore length, L_p is equal to the characteristic rock grain size, D_g. As such, the relationship between the effective pore radius, R_p and rock grain size, D_g is given in (14)

$$\frac{2\emptyset}{\mathrm{R_p}} = 6\frac{(1-\emptyset)}{\mathrm{D_g}} = 6\frac{(1-\emptyset)}{\mathrm{L_p}} \tag{14}$$

The grain size, $\mathrm{D_g}$ or $\mathrm{L_p}$ can be calculated as the representative grain size for a packed bed of mono-sized spherical particles using the Blake-Kozeny equation (Brakstad and Rosenkilde, 2016). Therefore, the pore residence time can be computed as shown in (15)

$$\tau_\mathrm{r} = \frac{\mathrm{L_p}}{v_p} = 12\left(\frac{1-\emptyset}{\emptyset\gamma}\right) \tag{15}$$

Where v_p is the average pore velocity and $\gamma = 4v_p/\mathrm{R_p}$ relates the shear rate at the wall to the average pore velocity. The elongational relaxation time, τ_el is computed as the characteristic time scale of diffusion and simplified as equation (16)

$$\tau_\mathrm{el} = \frac{36}{5}\left(\frac{\mu_\mathrm{s}[\mu]\mathrm{M_w}}{\mathrm{R_g T}}\right) \tag{16}$$

The onset of shear thickening is assumed to occur when the pore residence time is of the same magnitude as the elongational relaxation time. Therefore,

$$12\left(\frac{1-\emptyset}{\emptyset\gamma_c}\right) = \frac{36}{5}\left(\frac{\mu_\mathrm{s}[\mu]\mathrm{M_w}}{\mathrm{R_g T}}\right) \tag{17}$$

Simplifying,

$$\gamma_c = \frac{5}{3}\left(\frac{1-\emptyset}{\emptyset}\right)\left(\frac{\mathrm{R_g T}}{\mu_\mathrm{s}[\mu]\mathrm{M_w}}\right) \tag{18}$$

Equation (18) represents critical shear rate for the onset of shear thickening. However, this expression may not accurately calculate the shear rate at the onset of shear thickening. This is due to the uncertainties in the polydispersivity of polymers and the effect of polymer stretching. The relationship in (18) can be made to account for the effects of polydispersivity arising from hydrophobic interactions as follows.

$$\gamma_c = \lambda_\mathrm{b}\left(\frac{1-\emptyset}{\emptyset}\right)\left(\frac{\mathrm{T}}{\mu_\mathrm{s}[\mu]\mathrm{M_w}}\right) \tag{19}$$

Where $\lambda_b = 5R_g/3$ in this case. However, the effect of polymer stretching on hydrophobic interactions can be incorporated by establishing a relationship between the critical shear rate for the onset of shear thickening, γ_c, polymer relaxation time, λ_1 and the stretch rate, λ_{str} as shown below in (20)

$$\gamma_c = f(\lambda_1, \lambda_{str}) \tag{20}$$

A simple approach to establishing this relationship is based on the understanding that the critical shear rate, γ_c is the shear rate at which the shear thinning and shear thickening are equal. For a rheological model with shear thinning and thickening components, equating these components would allow for the prediction of γ_c taking into account λ_1 and λ_{str}.

3.4. Predicting the Onset of Shear Thickening using Rheological Models

Predicting the onset of various flow regimes associated with polymer flow in porous media is vital for designing chemical flooding operations. This is particularly significant for hydrophobically associating polymers where there are constrictions on polymer concentration and injectivity. The various flow regimes can be summarised by equations (21) – (23) below:

$$\lim_{\gamma \approx 0} \mu_{app} = \mu_0 \tag{21}$$

$$\lim_{\gamma \approx \gamma_c} \mu_{app} = \mu_{min} \tag{22}$$

$$\lim_{\gamma \approx \infty} \mu_{app} = \mu_{max} \tag{23}$$

Equation (21) simply refers to the Newtonian flow regime and the onset of shear thinning. In Equation (22), this marks the onset of shear thickening (where μ_{min} is the minimum viscosity) is provided whilst equation (23) refers to the maximum value for viscosity (μ_{max}) after which shear degradation sets in. Therefore, an apparent viscosity model describing the full spectrum of polymer flow in porous media should capture the highlighted regimes from equations (21) – (23). Studies on polymer flow in porous media have considered the onset of shear thickening and shear degradation as important to polymer flooding. For this review, predictive approach to the onset of shear thickening is considered. Most predictive models employed in the study of polymer flow have considered the use of the Deborah Number ($\mathrm{N_D}$) in predicting the onset of shear thickening. The Deborah Number is defined as the ratio of the polymer relaxation time (τ_r) to the characteristic time of flow (τ_p) as shown in Equation (24)

$$\mathrm{N_D} = \frac{\tau_\mathrm{r}}{\tau_\mathrm{p}} \tag{24}$$

Associating polymers with varying amounts of hydrophobic monomer will have a wide range of molecular weight leading to varied relaxation times. In estimating the onset of shear thickening, some researchers have recommended the use of the longest relaxation time in estimating $\mathrm{N_D}$ (Skauge, et al., 2018). However, the use of the longest relaxation time may lead to an overestimation of $\mathrm{N_D}$ at the onset of shear thickening. In addition to this, a wide range of $\mathrm{N_D}$ have been reported at the onset of shear thickening behaviour. The work of Heemskerk et al. (1984) captured this and reported that the use of different polymers in the same porous media yielded the same $\mathrm{N_D}$ and the reverse was the case when the same polymer was employed in different rocks leading to $\mathrm{N_D}$ values between 1 and 2. It was concluded that the concept of the $\mathrm{N_D}$ can only be used to give a first estimate of the critical flow rate, because of the inadequacy of calculating the stretching rate. Similarly, Zamani et al. (2015) reported that estimation of the stretch rate is crucial towards calculating the $\mathrm{N_D}$ at the onset of shear thickening. The authors proposed a linear function to relate the stretch rate to the Darcy velocity thereby obtaining the distribution of the stretch rate in the porous media. In summary, the use of relaxation time alone in calculating the onset of shear thickening is not sufficient if the stretch rate cannot be estimated. Accordingly, Lohne et al. (2017) reported that the use of $\mathrm{N_D}$ in describing the onset of shear thickening is limited as it only captures the insufficient relaxation time required to recover from its deformation arising from the previous pore throat entry. The reason for the adoption of $\mathrm{N_D}$ for predicting shear thickening is that the events of insufficient relaxation time for recovery and the characteristic time for flow in a pore entrance are assumed to be close (Lohne, et al., 2017). In other words,

$$\mathrm{N_D} = \frac{\tau_r}{\tau_p} \approx 1 \tag{25}$$

The model described by Delshad et al. (2008) is widely seen as a “unified model” which is applied to the full spectrum of flow of polymers in porous media. However, the constitutive equations (shear and elongational viscosity models) of the model were independently constructed for shear thinning and shear thickening. As a result, while the full spectrum of the polymer behaviour may be captured, its predictive capability for the various flow regimes as depicted by equations (21) to (23) may not be entirely captured. Table 2 shows the predictability of models developed by authors from Table 1 based on equations (21) to (23). The predictability of the proposed models by the various authors does not capture completely the three conditions. The proposed model by Hirasaki & Pope (1974) predicts at $\gamma \approx \infty$, an infinite value for the viscosity. In other words, the model cannot capture the onset of shear degradation. The same applies to the model proposed by Masuda et al. (1992) except at $\gamma \approx 0$. For the model by Delshad et al. (2008), it predicts μ_0 and μ_{max} for at $\gamma \approx 0$ and $\gamma \approx \infty$ respectively. This implies that it can describe the shear-thinning region and predicts the onset of shear degradation. The model by Stavland et al. (2010) predicts a value of μ_0 and ∞ at $\gamma \approx 0$ and $\gamma \approx \infty$ respectively. However, a critical issue that seems not captured is the prediction of the onset of shear thickening. A model for in-situ rheology should capture the prediction of the onset of shear thickening according to equation (22) when

$$\mu_{sh} = \mu_{el} \tag{26}$$

The model proposed by Stavland et al. (2010) estimates the critical shear rate for the onset of shear thickening as

$$\gamma_c = \frac{1}{\lambda_2} = N_D \left(\frac{1-\emptyset}{\emptyset}\right)\left(\frac{6\propto\sqrt{\tau}}{\lambda_1}\right) \tag{27}$$

Where γ_c is related to rock properties such as porosity, $\emptyset$, $\propto$ is a tuning parameter and tortuosity, τ. λ_1 and λ_2 are parameter constants. A similar expression was proposed by Lohne et al. (2017) for estimating the critical shear rate as shown in equation (28)

$$\lambda_2 = \frac{1}{\gamma_c} = \frac{1}{N_D^c}\left(\frac{3}{5R_g}\right)\left(\frac{\emptyset}{1-\phi}\right)\left(\frac{\eta_s[\eta]M_w}{T}\right) \tag{28}$$

However, there may not be a synergistic relationship between what can be obtained by Equation (26) and that estimated by equations (27) and (28). Applying equation (17) to the shear and elastic components of the unified viscosity model of Delshad et al. (2008) and Stavland et al. (2010) (see Table 1), it would be expected that shear rate value obtained when equated would approximate closely to the estimated values of (18) and (19) respectively. Nonetheless, equations (27) and (28) are dependent on the proper estimation of the Deborah number as it relates to the stretch rate as earlier mentioned. In addition, equating the elastic components and the shear components in order to obtain an expression for the critical shear rate may not yield an explicit expression. From the model of Delshad et al. (2008), this can only reduce to Equation (29)

$$\left[-\langle\lambda_2\tau_r\gamma\rangle^{(n_2-1)}\right] = \ln\left[1 - \frac{\mu_\infty+(\mu_0-\mu_\infty)\left(1+[\lambda_1\gamma]^2\right)^{(n_1-1)/2}}{\mu_{max}}\right] \tag{29}$$

As such, an explicit expression for the critical shear rate cannot be obtained and can only be achieved through a numerical solution and may not necessarily tally with values obtained from equations (27) or (28). Apart from relating the parameter constants of the model to the rock and polymer properties, there is a need for the model to satisfy equation (26) to really describe the full spectrum of polymer flow in porous media and predict the minimum viscosity before shear thickening sets in. Furthermore, the rheological models described in Table 2 do not have a parameter associated with the stretch rate of the polymer during in-situ flow in a porous media. There is need to simplify rheological models to account for the effect of polymer stretching on hydrophobic interactions. As such, establishing the actual form of equation (20) would be key in linking the effect of polymer stretching to hydrophobic interactions in a porous media. Besides this, most of the rheological models for in-situ flow of polymer in porous media

3.5. Degradation of Associating Polymers in Porous Media

The degradation of polymers has been reported under thermal, chemical and mechanical conditions (Brakstad and Rosenkilde, 2016; Lohne et al., 2017; Ferreira and Moreno, 2017). These conditions can take place in the form of high temperature (thermal conditions), high salinity and oxidative conditions (chemical conditions), fluid stresses in pumps, valves, injection wellbore, sand face (mechanical conditions) or any combination of the above (Brakstad and Rosenkilde, 2016). A parameter which is used in describing the degradation of polymer molecules is its molecular weight. Specifically, polymer chains rarely do have the same degree of polymerization and hence molecular weight. Therefore, there would always be a distribution of molecular weight around an average value due to some polymer chains being longer than the others. The molecular weight distribution describes the relationship between the number of moles of each polymer species and the molecular weight of that species using a discretized log-normal distribution (Brakstad and Rosenkilde, 2016). Hence, the degradation of polymers can be described as the scission of long-chain polymers when exposed to the degradation conditions mentioned earlier (Vanapalli et al., 2006; Zaitoun et al., 2012). According to Lohne et al. (2017), a simple model based on Figure 8 for the degradation study of polymers can be described using equation (30)

$$\frac{\mathrm{dM_w}}{\mathrm{dt}} = -f_{rup}\mathrm{M_w} \qquad (30)$$

Where $\mathrm{M_w}$ is the polymer molecular weight and f_{rup} is the polymer rupturing or degradation rate. Determination of the molecular weight of polymers require the use of the Huggins equation in (5) for the estimation of the intrinsic viscosity $[\mu]$ and this is related to the molecular weight using the Mark-Houwink equation. However, equation (5) is truncated after the second term depending on the value of the coil overlap parameter ($[\mu]c$). The coil overlap concentration refers to the polymer concentration where polymer coils begin to touch each other. According to Brakstad and Rosenkilde (2016), when the value of $[\mu]c$ is less than 5, equation (5) remains the expression for the Huggins equation. However, for associating polymers, modification of equation (5) is necessary to account for semi-dilute or concentrated conditions. Consequently, Brakstad and Rosenkilde (2016) indicated that higher order terms can be added to equation (5) when $4 < [\mu]c < 15$ as shown in (31)

$$\mu_0 = \mu_s + \mu_s(k_0[\mu]c + k_1[\mu]^2c^2 + \mathbf{k_2}[\boldsymbol{\mu}]^{\mathbf{3}}\mathbf{c}^{\mathbf{3.8}} + \cdots) \qquad (31)$$

The implication of this is that the effect of polymer intermolecular interaction on viscosity is taken into account with the higher order terms. For $[\mu]c > 15$, the Martin equation is used as shown in (32) to describe semi-dilute or concentrated regime. Here, the exponential term is used to capture the contribution of intermolecular association.

$$\mu_0 = \mu_s + \mu_s(k_0[\mu]c)\left(\mathbf{e}^{[\mathbf{bk_1}[\boldsymbol{\mu}]\mathbf{c}]}\right) \qquad (32)$$

As shown in Figure 8, the MWD of polymers differs under static and dynamic conditions. Therefore, discretization of equation (5) would allow for computation of changing coil overlap parameter of the polymer molecules during flow. Equation (33) shows a discretized form of equation (31).

$$\mu_0 = \mu_s + \mu_s\left(k_0 \sum_{i=0}^{n}\langle[\mu]_i c_i\rangle + k_1 \sum_{i=0}^{n}\langle[\mu]_i c_i\rangle^2 + \mathbf{k_2} \sum_{\mathbf{i=0}}^{\mathbf{n}}\langle[\boldsymbol{\mu}]_{\mathbf{i}}\mathbf{c_i}\rangle^{\mathbf{3.8}} + \cdots\right) \qquad (33)$$

Overall, this higher order form of the coil overlap parameter, $\langle[\boldsymbol{\mu}]_{\mathbf{i}}\mathbf{c_i}\rangle^{\mathbf{n}}$, can be used to indicate the degree of hydrophobic interaction between associating polymers and incorporated into the molecular weight distribution profile. This indicates that the intermolecular association has a multiplicative effect on polymer rheology. In addition, there is a need to integrate this degradation procedure in a suitable rheological model as the degree of hydrophobic interaction under static and dynamic conditions can be properly studied. As mentioned earlier, an important aspect of associative polymer research is how these hydrophobic interactions are sustained and propagated under dynamic conditions. Hence, a numerical approach remains a realistic method in the study of the dynamic nature of hydrophobic interactions during the flow of associating polymers in a porous media. However, there is still a need for a qualitative approach for real-time study of this phenomenon in porous media. An existing approach which could be adapted for this is to measure the rheological properties of produced polymers and compare it with properties before injection. Nevertheless, this may not be a representative of the real-time trend of hydrophobic interactions during flow in a porous media. Therefore, a numerical approach remains a viable option and should follow the schematic modified from Brakstad and Rosenkilde (2016) in Figure 9.

4. Solution Properties of Associating Polymers from Produced Fluids

The associated goal of a polymer flooding design is the reduction in the amount and cost of chemicals employed. In other words, the cost-effectiveness of a polymer flooding project design is crucial to its successful deployment and application. In addition, another identified challenge with polymer flooding design is the disposal of produced fluid containing the residual polymer. The associative characteristics of hydrophobically associating polymers have been evidently shown to maintain the viscous properties of such polymers above the critical aggregation concentration. However, Lu et al. (2010) postulated that the successful characterization and reuse of hydrophobically associating polymers in produced fluids mean that:

a) The phenomenon of hydrophobic association exists in porous media. Nevertheless, not mentioned by the authors, this is dependent on the extent to which it is propagated in a porous media. The propagation of associating polymers deep into a reservoir may affect the hydrophobic interactions between polymer chains (in-situ) and when produced (ex-situ).
b) The possibility of a change in the critical aggregation concentration of the produced associating polymer and what this change means on the solution properties of the polymer. These changes, if they occur, may be attributed to changes in the hydrophobe content when the polymer flows through the porous media.

Studies by Lu et al. (2010) have shown that hydrophobically associating polymers obtained from produced fluids have lower hydrophobic content compared to pre-flooding conditions. This indicates that the compositional homogeneity of the polymers is affected which further explains the reduced associative effect of the polymers. However, the CAC of the associating polymer from the produced fluid was similar to its pre-flooding value. Although the reported results show that hydrophobically associating polymers can be reused, however, the study did not indicate if such property can be maintained in deep reservoirs. In addition, the well spacing in most oil fields would require deep propagation of polymers before breakthrough of solutions from the producer well. Where the hydrophobic associative features are lost after flowing a short distance, its mobility control cannot be sustained far from the wellbore where most of the oil is displaced (Seright et al., 2011). Maintaining the enhanced viscous properties (long-term stability) and ensuring its propagation in porous media under varied reservoir conditions would have a profound effect on the solution properties of produced associating polymers.

5. Conclusion and Future Perspectives

Hydrophobically associating polymers are non-Newtonian fluids which exhibit a variety of rheological behaviour such as shear thinning, shear thickening and polymer degradation. Ultimately, the hydrophobic interactions between these polymer chains remain the unique distinguishing property. However, the phenomenon of hydrophobic interaction requires sophisticated mathematical modelling which becomes further complicated when considering in-situ polymer flow in porous media. Accurate prediction of in-situ hydrophobic interactions between polymer chains requires an understanding of the various uncertainties surrounding polymer polydispersivity and stretching. Existing polymer viscosity models applied in the context of flow in porous media are a combination of time-independent models with the addition of viscoelastic features. However, the scope of the predictive capability of the different flow regimes of some of these models is limited. For example, most of these models cannot predict the onset of shear thickening, rather it is estimated based on known parameters describing the solution properties of the polymer and the rock properties. While this estimation is not out of place, there is a need for synergy between what can be estimated by simple calculation and that which is predicted by a model. Furthermore, the level of intermolecular associative effect during flow in porous media cannot be adequately accounted for by these models. There is a need to incorporate this in an overall analytical procedure describing the flow of associating polymers in a porous media. Currently, existing viscosity models are considered too parameterized with non-linear regression of each parameter for proper flow description considered challenging and time consuming for simulation purpose. Therefore, incorporating the effects of hydrophobic interactions would require possibly simplifying the model to reduce parameterization. One solution to this is to express the time constants as a function of polymer and rock properties. This would minimize available model constants; however, there is need not to oversimplify a model as the accuracy of the prediction may be compromised. In addition, the susceptibility of the CAC of associating polymers to changes in the presence of oil field conditions needs to be captured in existing analytical models. Consequently, the following recommendations have been made based on the issues identified in this review:

a) Investigate the sustainability of the hydrophobic associative effect of these polymers during propagation in porous media while taking into consideration the sensitivity of the critical aggregation concentration to temperature, salinity/hardness and pH.
b) Evaluate the viscoelastic model developed in this work for the prediction of the various regimes for associative polymer flow in a porous media. This should ensure that there is synergy between what can be predicted and what can be estimated for the onset of hydrophobic interaction, shear thickening and polymer degradation.
c) Develop a mathematical correlation of critical aggregation concentration to oil field parameters (such as temperature, salinity/hardness and pH) and evaluate its suitability for predictive modelling.
d) Develop a qualitative approach to study the hydrophobic interactions between associative polymers under real-time flow conditions in a porous media. The results of this approach should be compared to the quantitative approach described in this article.
e) Examine the impact of hydrophobic interactions on polymer injectivity as measured by polymer concentrations above the critical aggregation concentration. An understanding of its effect on the onset of shear thickening in porous media is important and has the potential to be a key focus of research activities in this field.
f) Investigate the possibility of a change in the critical aggregation concentration of the produced associating polymer and what this change means on the solution properties of the polymer. While previous works have indicated no noticeable change in CAC, the work was limited to a particular associating polymer.

Nomenclature

Abbreviations

CAC	Critical Aggregation Concentration
EOR	Enhanced Oil Recovery
HPAM	Hydrolyzed Polyacrylamide
HAPAM	Hydrophobically Associating Polymer
OOIP	Original Oil in Place
RF	Resistance Factor

Symbols

α	Tuning Parameter
$\mathrm{C_c}$ or C^*	Critical Aggregation Concentration
$\mathrm{C_s}$	Salinity Concentration
$\mathrm{c_p}$	Polymer Concentration
$\Delta\mathrm{C_s}$	Salinity Concentration Difference
$\mathrm{c_i}$	Concentration of the i^{th} Polymer Specie
f_{rup}	Polymer Degradation or Rupturing Rate
h	Elongation Constant
$\mathrm{R_g}$	Gas Constant
$\mathrm{K_1}$, $\mathrm{K_2}$,	Parameter Constants similar to Consistency Index from the Power Law Model
$\mathrm{k_0}, \mathrm{k_1}, \mathrm{k_2}$	Parameter Constants
$\mathrm{k_m}$	Model Parameter
$\mathrm{L_p}$	Pore Length
$\mathrm{D_g}$	Rock Grain Size
$\mathrm{N_D}$	Deborah Number
$\mathrm{N_D^c}$	Critical Deborah Number

$\mathrm{M_w}$	Molecular Weight
$\mathrm{n_1}$, $\mathrm{n_2}$	Parameter Constants similar to Flow Index from the Power Law Model
$\mathrm{N_D}$	Deborah Number
$\mathrm{N_a}$	Avogadro’s Number
T	Temperature
$\emptyset$	Porosity
$\Delta\mathrm{T}$	Temperature Difference
$\mathrm{T_o}$	Reference Temperature
τ_r	Polymer Relaxation Time
τ_p	Polymer Characteristic Time Flow
$[\mu]$	Intrinsic Viscosity
$[\mu]_i$	Intrinsic Viscosity of the i^{th} Polymer Specie
μ_0	Polymer Viscosity at Zero Shear Rate
μ_s	Solvent Viscosity
μ_sp	Polymer Specific Viscosity
μ_∞	Polymer Viscosity at Infinite Shear Rate for Shear Thinning
μ_max	Maximum Polymer Viscosity for Shear Thickening
μ or η	Polymer Viscosity
μ_app	Apparent Viscosity of Polymer in Porous Media
μ_sh	Shear Thinning Viscosity in Porous Media
μ_el	Elongational Viscosity or Shear Thickening Viscosity in Porous Media
$\mathrm{V_m}$	Volume Occupied per Polymer Chain
v_p	Average Pore Velocity
γ	Shear Rate
η_s	Solvent Viscosity

R_p	Effective Pore Radius
λ_1, λ_2	Model Constants
λ_a	Tuning Parameter
λ_b	Tuning Parameter
λ_{str}	Polymer Stretch Rate
$\bar{S}_{sw}$	Average Shear Stress
$\dot{\gamma}_a$	Apparent Shear Rate
γ_o	Initial Critical Rate
γ_c	Critical Shear Rate
γ_m	Third Critical Rate

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Conflict of Interest

The authors have no conflict of interest to declare regarding the publication of this manuscript.

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Figure 1*: Viscosity behavior of hydrophobically associating polymers (HAPAM) before and after the critical aggregation concentration.*

Figure 2*: Fluid element (A) under deformation (a) shear flow (b) extensional flow (Zamani et al., 2015)*

Figure 3*: A typical plot of viscosity versus shear rate for a polymer solution that exhibits shear thickening.* γ_c *is the first critical shear rate which marks the onset of shear thinning. The increase in viscosity begins at the critical shear rate* γ_c*, after a minimum viscosity,* μ_{min} *and shear thinning resumes after shear rate,* γ_m *at maximum viscosity,* μ_{max}*.* μ_o *represent polymer viscosity at low shear rate.*

Figure 4*: Interfacial tension of a 1000 mg/L ASP flooding system containing (a) HAPAM and (b) HPAM (Feng et al. 2013).*

Figure 5*: Core flooding results for the ASP system containing associative polymer as studied by Feng et al. (2013).*

Figure 6*: The effect of alkali on the viscosity of the associating polymer solution (Feng et al., 2013)*

Figure 7*: The effect of alkali mixed surfactant on the status of the associating polymer solution (Feng et al., 2013)*

Figure 8*: Flow of a polymer with its Molecular Weight Distribution (MWD) at the inflow, in a porous media and outflow. The thick square box represents the porous media with the changing MWD of the polymer subject to changing flow conditions.*

Figure 9*: A flow chart showing a proposed numerical approach to study of hydrophobic interaction between associating polymers during flow in a porous media.*

***Table 1**: Proposed models for polymer flow in porous media. Modified from (Skauge et al., 2018)*

Model Form	**Shear Component (μ_{sh})**	**Elastic Component (μ_{el})**	**Comment**	**Reference**
$\boldsymbol{\mu_{app} = \mu_{sh}(\mu_{el})}$	$\mu_{sh} = Hu^{n-1}$	$\mu_{el} = \frac{1}{1 - N_D}$	The model predicts an infinite value for the elongation viscosity with increasing Deborah Number, N_D	(Hirasaki and Pope, 1974)
$\boldsymbol{\mu_{app} = \mu_{sh}(\mu_{el})}$	$\mu_{sh} = \frac{\bar{S}_{sw}}{\dot{\gamma}_a}$	$\mu_{el} = C(N_D)^{m_c}$	$\bar{S}_{sw}$ is average shear stress at wall of channels, $\dot{\gamma}_a$ apparent shear rate in porous media. C and m_c are parameter constants	(Masuda et al., 1992)
$\boldsymbol{\mu_{app} = \mu_{sh} + \mu_{el}}$	$\frac{\mu_{sh} - \mu_\infty}{(\mu_0 - \mu_\infty)} = (1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}$	$\mu_{el} = \mu_{max}(1 - e^{[-\langle\lambda_2\tau_r\gamma\rangle^{(n_2-1)}]}$	This particular model was able to predict a maximum value for μ_{el} ($\mu_{el} = \mu_{max}$)	(Delshad et al., 2008)
$\boldsymbol{\mu_{app} = \mu_{sh} + \mu_{el}}$	$\frac{\mu_{sh} - \mu_\infty}{(\mu_0 - \mu_\infty)} = (1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}$	$\mu_{el} = (\lambda_2\gamma)^m$	m is the elongation exponent, ${}^1/_{\lambda_2}$ marks the onset of shear-	(Stavland et al., 2010)

		thickening

Table 2: *Predictive capability of various proposed models for in-situ rheology of polymers in porous media*

Model Form	$\lim\limits_{\gamma\approx 0} \mu_{app}$	$\lim\limits_{\gamma\approx\gamma_c} \mu_{app}$	$\lim\limits_{\gamma\approx\infty} \mu_{app}$
$* \mu_{app} = \left[\mu_\infty + (\mu_0 - \mu_\infty)(1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}\right]\left[\frac{1}{1-\tau_r\gamma}\right]$ (Hirasaki and Pope, 1974)	μ_0	-	∞
$* \mu_{app} = \left[\mu_\infty + (\mu_0 - \mu_\infty)(1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}\right][C(\tau_r\gamma)^{m_c}]$ (Masuda et al., 1992)	0	-	∞
$**\mu_{app} = \left[\mu_\infty + (\mu_0 - \mu_\infty)(1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}\right] + \left[\mu_{max}(1 - e^{\left[-\langle\lambda_2\tau_r\gamma\rangle^{(n_2-1)}\right]}\right]$ (Delshad et al., 2008)	μ_0	-	μ_{max}
$**\mu_{app} = \left[\mu_\infty + (\mu_0 - \mu_\infty)(1 + [\lambda_1\gamma]^2)^{(n_1-1)/2}\right] + [(\lambda_2\gamma)^m]$ (Stavland et al., 2010)	μ_0	-	∞

*Carreau model for shear thinning added to the elongational (or extensional) models by Hirasaki and Pope (1974) and Masuda et al. (1992). The Deborah number, $N_D = \tau_r\gamma$ for the extensional models

**Models by Delshad et al. (2008) and Stavland et al. (2010). For Stavland et al. (2010), $\gamma_c = {}^{1}/_{\lambda_2}$

Highlights

- Sustainability of hydrophobic interactions between associative polymers in porous media.
- Modelling the variation in hydrophobic interactions arising from reservoir conditions.

Shear thickening of associative polymers arising from hydrophobic interactions.

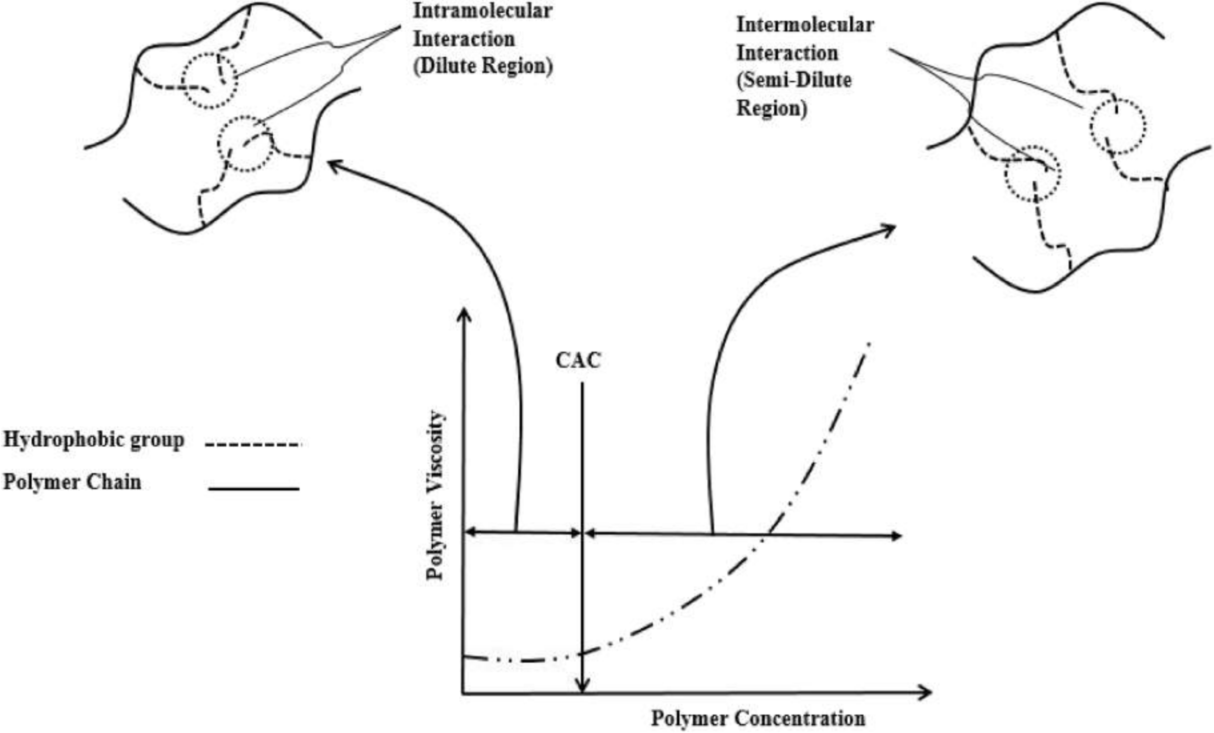

Intramolecular
Interaction
(Dilute Region)
Intermolecular
Interaction
(Semi-Dilute
Region)
CAC
Hydrophobic group
Polymer Chain
Polymer Viscosity
Polymer Concentration

Figure 1

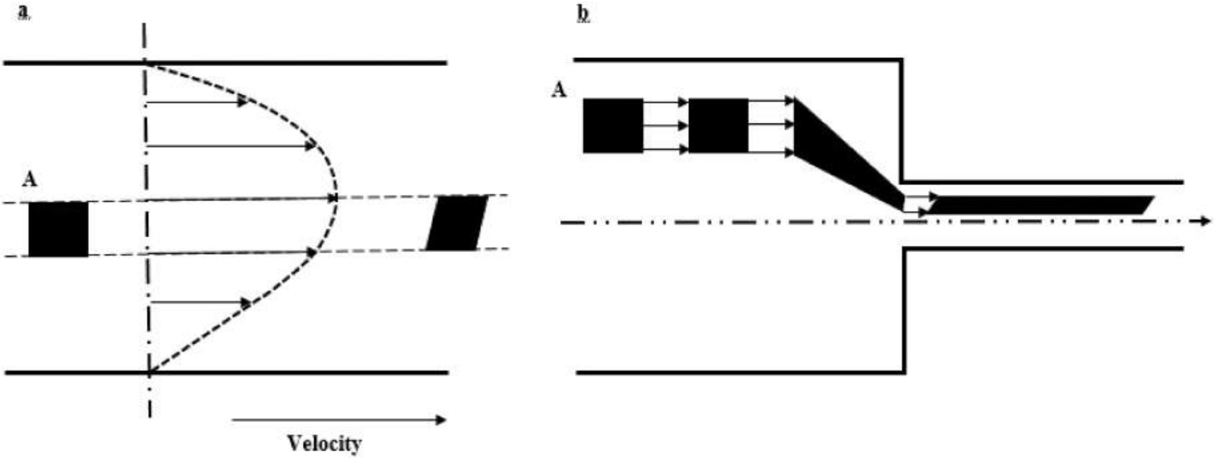


Figure 2

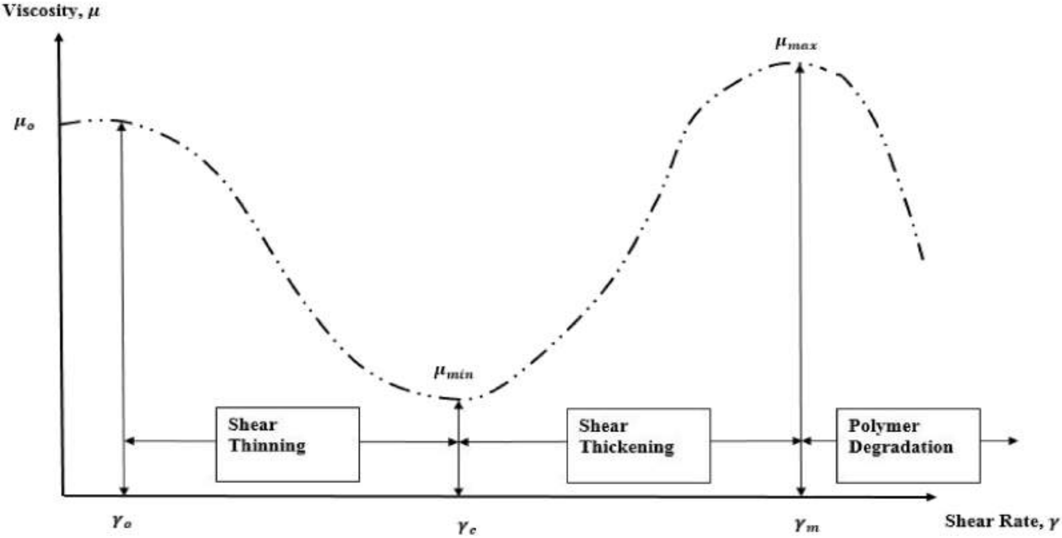

Viscosity, μ
μ_o
μ_{max}
μ_{min}
Shear Thinning
Shear Thickening
Polymer Degradation
γ_o
γ_c
γ_m
Shear Rate, γ

Figure 3

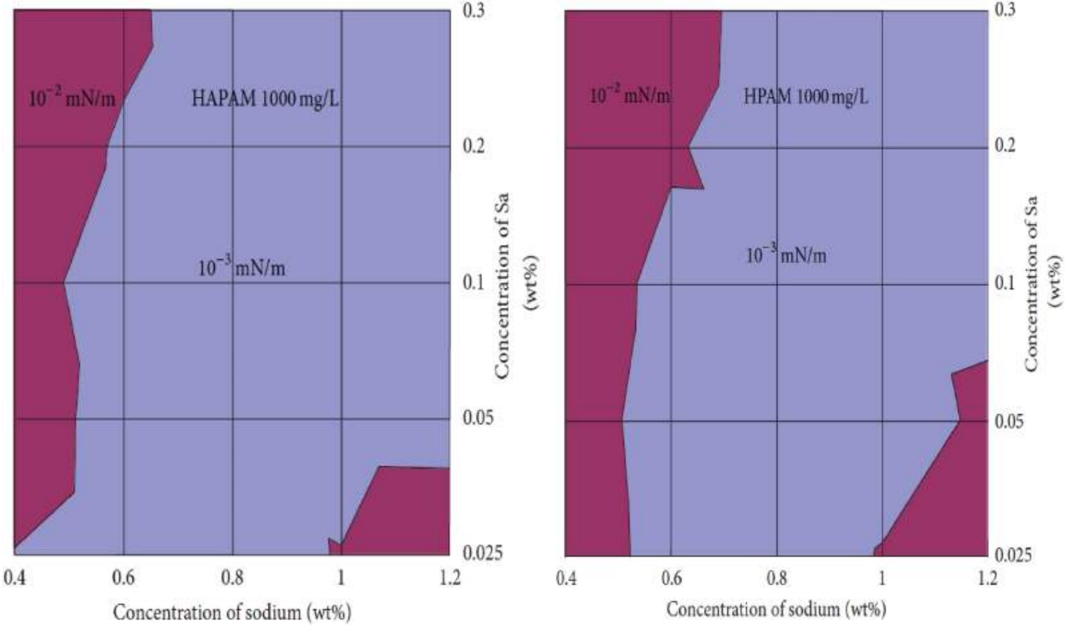
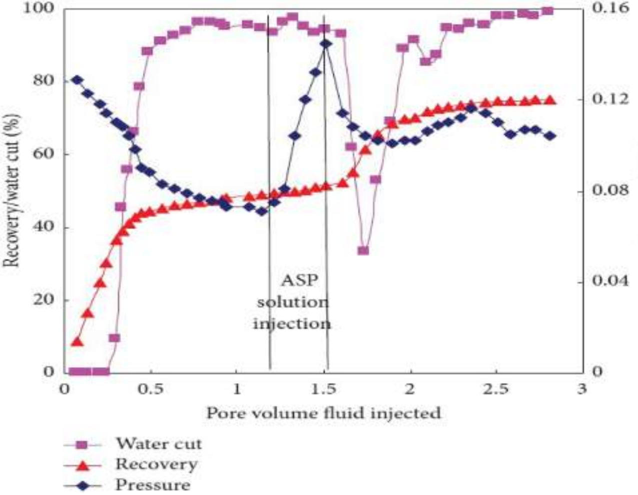
10^-2 mN/m
HAPAM 1000 mg/L
10^-3 mN/m
0.3
0.2
0.1
0.05
0.025
Concentration of Sa (wt%)
0.4
0.6
0.8
1
1.2
Concentration of sodium (wt%)
10^-2 mN/m
HPAM 1000 mg/L
10^-3 mN/m
0.3
0.2
0.1
0.05
0.025
Concentration of Sa (wt%)
0.4
0.6
0.8
1
1.2
Concentration of sodium (wt%)

Figure 4



100
80
60
40
20
0
Recovery/water cut (%)
0.16
0.12
0.08
0.04
0
Pressure (MPa)
ASP
solution
injection
0
0.5
1
1.5
2
2.5
3
Pore volume fluid injected
Water cut
Recovery
Pressure

Figure 5

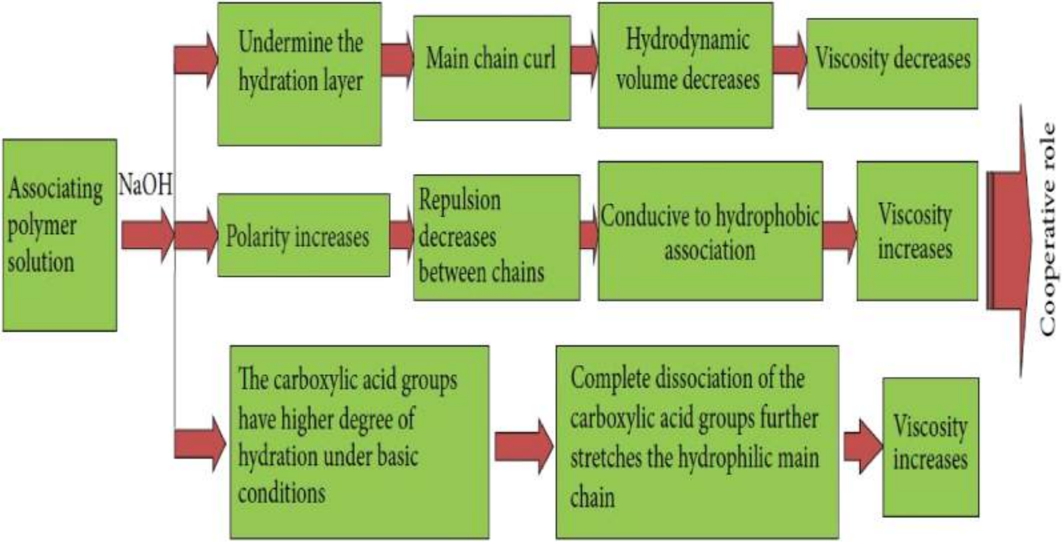
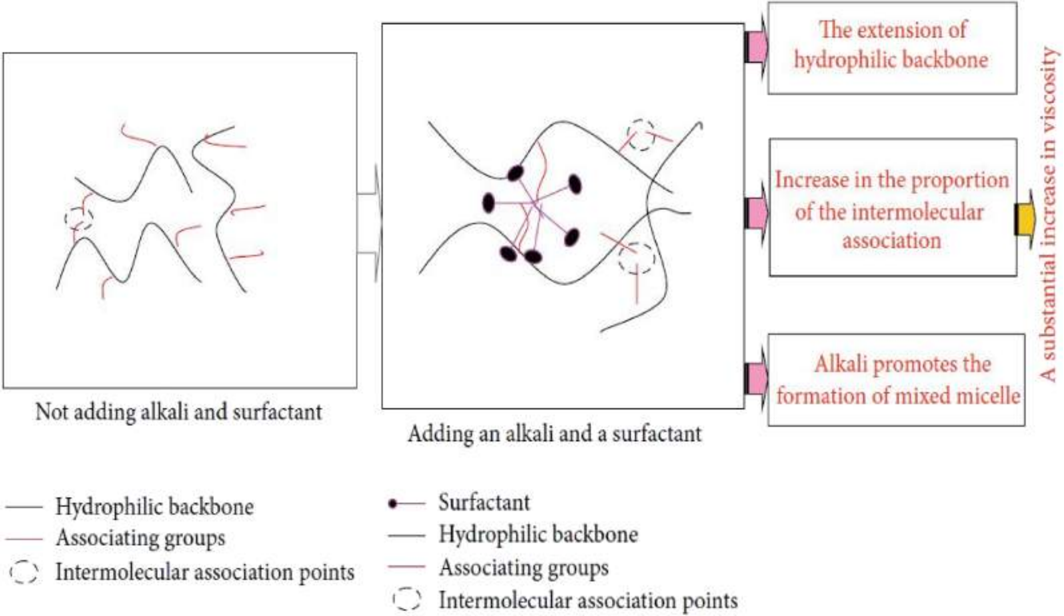

Associating polymer solution
NaOH
Undermine the hydration layer
Main chain curl
Hydrodynamic volume decreases
Viscosity decreases
Polarity increases
Repulsion decreases between chains
Conducive to hydrophobic association
Viscosity increases
The carboxylic acid groups have higher degree of hydration under basic conditions
Complete dissociation of the carboxylic acid groups further stretches the hydrophilic main chain
Viscosity increases
Cooperative role

Figure 6



Not adding alkali and surfactant
Adding an alkali and a surfactant
The extension of hydrophilic backbone
Increase in the proportion of the intermolecular association
Alkali promotes the formation of mixed micelle
A substantial increase in viscosity
Hydrophilic backbone
Associating groups
Intermolecular association points
Surfactant
Hydrophilic backbone
Associating groups
Intermolecular association points

Figure 7

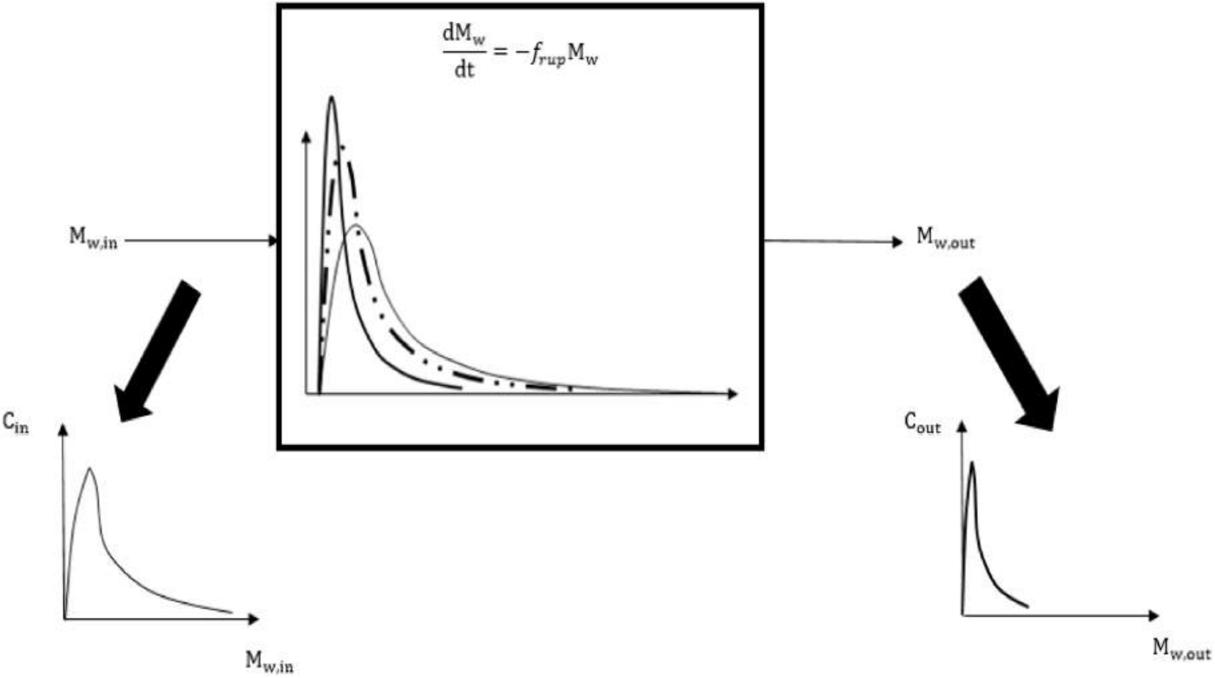


Figure 8

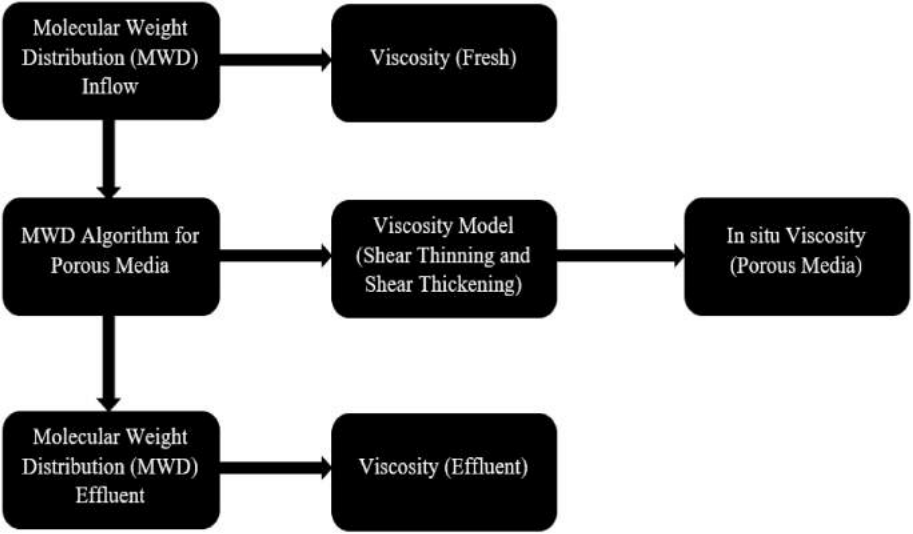

Molecular Weight Distribution (MWD) Inflow
Viscosity (Fresh)
MWD Algorithm for Porous Media
Viscosity Model (Shear Thinning and Shear Thickening)
In situ Viscosity (Porous Media)
Molecular Weight Distribution (MWD) Effluent
Viscosity (Effluent)

Figure 9