Assessment of solubility and viscosity of ultra-high molecular weight polymeric thickeners in ethane, propane and butane for miscible EOR

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Abstract

Natural gas liquid (NGL), a mixture consisting primarily of ethane, propane, and butane, is an excellent enhanced oil recovery (EOR) solvent. However, NGL is typically about ten times less viscous than the crude oil within the carbonate or sandstone porous media, which causes the NGL to finger through the rock toward production wells resulting in low volumetric sweep efficiency in five-spot patterns or during a linear drive displacement. The viscosity of candidate polymeric NGL thickeners is measured with a windowed, close-clearance falling ball viscometer, and an expression for the average shear rate associated with this type of viscometer is derived. High molecular weight polydimethyl siloxane

(PDMS, M_w $9.8 \cdot 10^5$) can thicken ethane, propane and butane, but the viscosity enhancement is very modest (e.g. a doubling of butane viscosity with 2% PDMS at 7 MPa and 25°C), making field application of PDMS unlikely. A dilute concentration of a drag-reducing agent (DRA) poly- α -olefin that has an average molecular weight greater than $2.0 \cdot 10^7$ is more promising as a potential thickener for liquid butane, liquid propane and liquid or supercritical ethane. The DRA polymer, which is introduced as an extremely viscous 1% or 2% solution in hexane, is soluble in butane and propane at 25-60°C and concentrations up to at least 0.5wt% at pressures slightly above the vapor pressure of butane or propane. The DRA polymer is much more difficult to dissolve in ethane, however, requiring pressures of more than 20 MPa. The DRA polymer is especially effective for thickening butane (e.g. a 4.8-fold viscosity increase at 25°C, 55.16 MPa and 0.2wt% DRA). The DRA is less effective for increasing propane viscosity (e.g. a 2.3-fold viscosity increase at the same conditions), and even less effective for thickening ethane. In general, viscosity enhancement increases with decreasing temperature, increasing pressure, and an increase in the carbon number of the light alkane, which are reflective of increased NGL solvent strength at low temperature and high pressure. Practical application of DRA during EOR may be hindered, however, by the relatively high concentration (~5000 ppm) of DRA polymer required for order-of-magnitude viscosity increases, very high pressure requirements for DRA dissolution if the ethane content of the NGL is high, and the large amount of hexane that would have to be introduced if the DRA polymer if it is introduced as a solution in hexane.

Keywords: Ethane, propane, butane, thickener, ultrahigh molecular weight polymer, poly- α -olefin

1. Introduction

According to a report published by Oil & Gas Journal in 2014 (Koottungal, 2014), hydrocarbon miscible enhanced oil recovery (EOR) has contributed 1.5-2.0% of overall oil production in US over the past several decades. Hydrocarbon miscible flooding typically involves the injection of natural gas liquids (NGL) (Taber, 1983), a mixture of ethane, propane, butane and a small amount of higher alkanes. This

48 mixture is an excellent solvent for the displacement of oil because it often exhibits complete miscibility
49 with crude oil at reservoir conditions (i.e. first contact miscibility). Therefore NGL is a better solvent
50 than CO₂ for oil recovery from shallow reservoirs at relatively low pressures because NGL can develop
51 first contact miscibility with crude oil at much lower pressures than the minimum miscibility pressure
52 associated with CO₂, which is more commonly used in deeper, higher pressure formations.

53 Hydrocarbon miscible EOR is not as pervasive in the United States as CO₂ EOR because most of the
54 CO₂ is obtained from massive natural deposits and is transported through extensive CO₂ distribution
55 pipelines, whereas the NGLs used for EOR originate in gas processing plants associated with oil
56 recovery projects (including CO₂ EOR). NGLs are more expensive than CO₂ and this impacts the
57 operating costs and economic viability of the hydrocarbon miscible displacement process. Further, there
58 are markets for NGLs other than for its implementations as an oil recovery solvent; it may be sold for its
59 fuel value (e.g. LPG blends of propane and butane) or for the use as a raw material in the manufacture of
60 chemicals (e.g. cracking ethane to make ethylene). Nonetheless, when there are no nearby markets for
61 NGLs, it can be economical to use NGLs for hydrocarbon miscible EOR. CO₂ miscible and immiscible
62 displacement processes leave substantial amounts of CO₂ behind in the formation, which serves to
63 sequester CO₂. This geologic sequestration will become increasingly important mode of CO₂ disposal
64 as anthropogenic sources of CO₂ used for EOR become a more significant fraction of the CO₂ supply.
65 However, the NGL left behind in the formation serves solely as an economic loss of solvent.

66 Although the solvent strength of an NGL mixture is exemplary even at relatively low pressures in
67 shallow reservoirs, this fluid has the same two fundamental disadvantages as CO₂; low density and
68 viscosity relative to crude oil. The density of CO₂ at MMP ranges from roughly 500-700 kg/m³ (Enick
69 et al., 1988; Holm and Josendal, 1982). The density of high pressure NGL at typical hydrocarbon
70 miscible conditions is roughly 500 kg/m³. At EOR conditions (i.e. T = 20 - 80°C, P = 2.5 - 14.0 MPa)
71 ethane, propane and butane have densities of roughly 400 kg/m³, 500 kg/m³ and 600 kg/m³ respectively

(Friend et al., 1991; Miyamoto and Watanabe, 2000, 2001). Because the NGL density value is less than that of crude oil, NGLs tend to exhibit gravity override as they flow from injections wells through horizontal formations into production wells, reducing oil recovery in the lower portions of reservoir. It is not possible to substantially increase the density of NGL with a dilute concentration of an additive, however.

The viscosity of CO₂ or NGLs at reservoir conditions is roughly 0.05 mPa s and 0.1 mPa s, respectively; values that can be significantly lower than brine and oil viscosity. For example, the range of crude oil viscosity values associated with most hydrocarbon miscible projects in the US is 1-2 mPa s, but several fields contain crude oil with a viscosity of 7-140 mPa s. In Canada, crude oil viscosity values in hydrocarbon miscible projects range between 0.1 – 0.8 mPa s (Koottungal, 2014). The low viscosity of NGL relative to the crude oil being displaced leads to an unfavorable mobility ratio which, in turn, can result in viscous fingering, early NGL breakthrough, high NGL utilization ratios, high gas-to-oil ratios in production wells, and poor sweep efficiency in a five spot or linear drive (Claridge, 1972; Habermann, 1960). These effects can be mitigated, however, if a gravity-assisted top-down displacement process that takes advantage of the density difference to suppress fingers can be implemented. Further, in stratified formations, the viscosity contrast enhances the flow of NGLs into high permeability zones that contain little recoverable oil.

It is possible to diminish the mobility of dense NGL via the water-alternating gas (WAG) injection process, where slugs of NGL and brine are injected alternately. As these fluids mix within the porous medium while flowing toward the production well, the saturation (i.e. volume fraction of NGL in the pores) is decreased by the presence of the injected brine, thereby reducing the relative permeability of the NGL (Stalkup, 1983). The objective of this study, however, is to determine if one can reduce NGL mobility by increasing the viscosity of NGLs using dilute concentrations of high molecular weight polymers. Polymeric thickeners for ethane, propane, butane are intended to dissolve completely in these

high pressure fluids, forming a transparent, thermodynamically stable, single-phase solution capable of flowing through porous media. The viscosity of this solution can be tailored to match that of the crude, primarily by adjusting the concentration of the polymer in the NGL. This could result in a dramatic improvement in mobility control and the elimination of the need for the WAG process.

It is common to use high molecular weight oil-soluble polymers to thicken conventional oils and hydrocarbons that are liquids at ambient pressure, for example during the manufacture of lubricants (Rudnick, 2009). However, challenges arise as one assesses polymeric thickeners for butane, propane and ethane because high pressure equipment is required for testing. Further, these light alkanes become increasing poor solvents for polymers as one progresses to from pentane to ethane.

There have been reports of dissolution of high molecular weight polymers in NGLs, such as polyethylene Mw (weight-average molecular weight) 1.08×10^5 in ethane (Ehrlich and Kurpen, 1963), polyethylene Mw 3.4×10^5 in propane (Meilchen et al., 1991), polyethylene Mw 4.2×10^5 in butane (Xiong and Kiran, 1994); poly(ethylene-co-methyl acrylate) Mw 1.0×10^5 in ethane (Hasch et al., 1992), poly(ethylene-co-methyl acrylate) Mw 1.4×10^5 in propane and butane (Pratt et al., 1993); poly(ethylene-co-octene) Mw 2.0×10^5 in propane (Whaley et al., 1997); polypropylene Mw 2.1×10^5 in propane (Chen et al., 1995); and poly(ethylene-co-acrylic acid) Mw 1.0×10^5 in propane and butane (Lee et al., 1994).

With regard to the highest molecular weight polymers, polyisobutylene Mv (viscosity average molecular weight) 1.66×10^6 is slightly soluble in compressed liquid butane, but is insoluble in propane and ethane (Zeman et al., 1972). A trimethyl silyl-terminated polydimethyl siloxane Mv 6.26×10^5 is soluble in ethane, propane and butane, with the highest pressures being required for dissolution in ethane and the lowest pressures being required for butane (Zeman et al., 1972).

There are no reports of ethane being thickened with polymers. There are a few reports of propane and butane being thickened with polymers, however. For example, in the late 1960's, several patents were published citing the advantages of thickening liquid propane with dissolved polymers (Henderson et al.,

1967; Roberts et al., 1969). For example, Dauben and co-workers studied polyisobutylene polymer (PIB, Mw 1.3×10^5) in a solution of propane (75 vol%) and a heptane-rich condensate (25 vol%) and this patent claimed to achieve a 2-3 fold viscosity enhancement at 0.25wt% polymer (Dauben et al., 1971). However, the method used for measuring the viscosity was not reported. While studying various polymers for CO₂ and NGL thickening, Heller and co-workers found poly α -olefins based on *n*-decene, *n*-pentene, *n*-hexene to be only sparingly CO₂-soluble, but quite soluble in liquid *n*-butane. A 5-fold viscosity enhancement for liquid butane was measured with a falling cylinder viscometer with these polymers at concentrations of 2.2 wt% (Dandge and Heller, 1987). They did not report testing of these polymers in liquid propane or in ethane.

The objective of this work is to assess the solubility of high and ultra-high molecular weight oil soluble polymers in NGL constituents and to determine the viscosity of NGL solutions containing dilute concentrations of the polymer. We have focused our efforts on polymeric materials that have been employed as a drag reducing agent (DRA) in oil pipelines (Ultrahigh molecular weight polyacrylamide is water-soluble but NGL-insoluble, therefore it was not considered). DRA polymers typically have ultra-high molecular weights greater than 1.0×10^7 and are often used in concentrations of only 1-20 ppm to attain substantial increases in throughput at a specified pressure drop or significant power reduction for a specified volumetric flow rate. At these dilute concentrations, the polymers do not significantly change the fluid properties; therefore the viscosity of the solution of oil and dissolved DRA at a concentration of 1-20 ppm as measured in a laminar flow viscometer will be essentially the same as the oil. During turbulent flow in pipelines with rough inner surfaces, these polymers act like buffers in the fluid layer adjacent to the inner pipe wall to decrease the amount of energy lost in the formation of turbulent eddies (Abubakar et al., 2014). In general, the higher the molecular weight of the polymer, the smaller the concentration required to achieve a targeted level of drag reduction. Therefore DRA polymers with molecular weights in excess of 5×10^6 g/mol are particularly well suited for drag reduction

(Milligan et al., 2009). Polymers that have been studied as DRAs for organic liquids include polydimethyl siloxane (PDMS), poly- α -olefins (of hexene, octene, decene, dodecene), polyethylene, polyethylene terephthalate, polyethylene oxide, polyisopropene, polyisobutylene (PIB), polybutadiene, ethyl cellulose, ethylene-vinyl alcohol copolymer, and epichlorohydrin-ethylene oxide copolymers (Burger et al., 1980; Canevari and Peruyero, 1970; Evans, 1974; Liaw, 1968; Ma et al., 2003). In this work high molecular weight poly- α -olefin, PDMS, and PIB are assessed for their ability to increase the viscosity of ethane, propane and butane.

Because the intent of this work is to increase viscosity at laminar flow conditions with low concentrations of a high or ultra-high molecular weight polymer, polymer concentrations significantly greater than those used for drag reduction in pipelines are expected to be required.

2. Material

Attempts to rapidly dissolve polymeric DRAs in hydrocarbons with intense mixing results in shear-based chain scission of the polymer and hence a loss in its drag reducing or thickening capability. However, prolonged mixing at low rpm in a high pressure phase behavior cell and viscometer is not practical. Therefore pre-made 1 wt% and 2 wt% solutions (designated as DRA-1% and DRA-2%) of an ultra-high molecular weight poly- α -olefin DRA polymer in hexane were obtained from a commercial source (LiquidPower™ Flow Improver from Lubrizol Specialty Products, Inc., Houston, TX) and used as received (i.e. Samples of pure poly- α -olefin were not used in this study). The precise polymer composition is proprietary, but the polymer is a poly- α -olefin with an average molecular weight greater than 2.0×10^7 ; the molecular weight of this hydrocarbon-based polymer was not confirmed in our laboratory. Each solution prepared with DRA-1% or DRA-2% therefore contains 99 or 49 times, respectively, as much hexane as the ultra-high molecular weight poly- α -olefin DRA on a weight basis. The poly- α -olefin is referred to as DRA in the rest of the paper.

n-hexane (Laboratory grade, >95% purity), which was used as a co-solvent in some of the experiments involving PIB, was obtained from Sigma Aldrich, Pittsburgh PA and used as received.

An ultrahigh molecular weight PIB, M_w 1.0×10^7 (Oppanol B250), was obtained from BASF Corporation, Florham Park, NJ and this rubbery solid polymer was used as received. The molecular weight of this hydrocarbon-based polymer was not confirmed in our laboratory. PIB, M_w 1.0×10^7 is referred to as PIB in the rest of this paper.

A silanol-terminated PDMS (Silanol SE 30, M_w 9.8×10^5) was obtained from Momentive, Schenectady, NY and was used as received. The Momentive Silanol product is, to the best of our knowledge, the highest molecular weight commercially available polydimethyl siloxane polymer. Weight-average molecular weight (M_w) values for these silicone polymers were measured by a Gel Permeation Chromatography (GPC) technique at GE Global Research, Niskayuna, NY. The silanol-terminated PDMS, M_w 9.8×10^5 , is referred to as PDMS in the rest of this paper.

Ethane, propane and *n*-butane were purchased from Matheson Tri-gas, West Mifflin, PA with a purity level of 99.99% and used without further purification.

3. Experimental

3.1 Polymer preparation

In some experiments, the PIB polymer that was to be dissolved in ethane, propane or butane was added in its pure form. In other experiments, a 1wt% solution of PIB in hexane was prepared with a magnetic stirplate by combining small chunks of PIB, hexane and a magnetic stirbar in a sealed beaker and stirring for 24 hours at room temperature ($\sim 23^\circ\text{C}$). This yielded a transparent, homogeneous, extremely viscous liquid solution. The hexane was intended to act as a co-solvent that would facilitate the dissolution of dilute concentrations of PIB in the dense alkane.

189 The high molecular weight PDMS, a viscous liquid, was used as received. Because it proved to be
190 soluble in the NGL components without the need for a co-solvent, the PDMS was not combined with a
191 co-solvent in order to enhance solubility in any experiments.

192 The 1wt% and 2wt% solutions of the ultra-high molecular weight poly- α -olefin in hexane were used as
193 received, therefore in all experiments involving dissolution of the DRA polymer in ethane, propane or
194 butane, the final solution contained 49-times or 99-times as much hexane as DRA polymer, respectively.

195 No attempt was made to separate the DRA polymer from the LiquidPower™ Flow Improver solution of
196 DRA in hexane provided by Lubrizol Specialty Products.

197 3.2 High pressure phase behavior measurement

198 Standard non-sampling techniques for visually determining the cloud point of mixture with known
199 overall composition with an invertible, variable volume cell were employed. Details of the phase
200 behavior measurement are provided elsewhere (Hong et al., 2008; Kilic et al., 2003; Miller et al., 2009),
201 and an illustration of the solubility experiment is provided in **Fig. 1**.

Fig. 1. Experimental procedure for polymer solubility in high pressure fluid: (a) load polymer (b) displace air (c) add NGL component to expand sample volume (d) isolate mixture, stir, dissolve, heat, and compress to very high pressure until a single phase is attained (e) slowly expand sample volume to record cloud point

First, (Fig. 1a) a specified amount of pure PIB, pure PDMS, a 1wt% solution of PIB in hexane, a 1wt% DRA polymer solution in hexane, or a 2wt% solution of PIB in hexane is added to the (0-100 ml) sample volume housed within a thick-walled Pyrex tube that is inserted into the open, windowed phase behavior cell at ambient temperature and pressure. The top of the phase behavior cell, which has an impeller and a port for the addition/removal of fluids to/from the sample volume, is then bolted to the body of the cell, sealing the top of the sample volume. The cylindrical sample volume is then reduced by using a positive displacement (PD) pump to force a transparent overburden fluid into the cell (Fig. 1b), which causes the floor of the sample volume (a sliding piston with an O-ring around its perimeter) to slide upward while maintaining the seal. The volume is reduced until the polymer is nearly touching

the impeller blades at the top of the cell. This action displaces the air from the sample volume and reduces the vapor space around the polymer sample to its smallest possible value. The small vapor space of the sample volume is then flushed three times with low pressure ethane, propane or butane. High pressure liquid ethane, propane or butane is then displaced from the second PD pump into the sample volume at the exact same volumetric rate that the sample volume is expanded by withdrawing the overburden fluid into the first PD pump, (Fig. 1c), resulting in a well-controlled, essentially isothermal and isobaric addition (typically 23°C and 10.34 MPa) of a specified volume of the NGL component into the expanding sample volume. The density of the NGL component at the temperature and pressure of the positive displacement pump are known, therefore the density of the fluid can be determined from NIST data (NIST Chemistry Webbook, 2016). The product of the density and the precise volume of NGL component added to the cell is the mass of the NGL in the mixture. After the desired amount of NGL component is introduced to the sample volume, a valve at the top of the sample volume is closed to isolate the mixture of known overall composition. The mixture of polymer and NGL component (and hexane, if present) is then mixed with a magnetically driven slotted blade impeller at a specified temperature pressure in an attempt to attain a single transparent, homogeneous, stable solution. Mixing can be conducted at pressures up to 69 MPa in an attempt to facilitate dissolution. This increase in pressure is accomplished by using the second PD pump to force the overburden fluid into the phase behavior cell, (Fig. 1d) which pushes the sliding piston upward, thereby reducing the size of the cylindrical sample volume. The thickener and alkane are mixed for up to six hours at pressures as high as 69 MPa when attempting to dissolve the polymer in the alkane. Whether the polymer is a liquid or a solid, one look into the windowed cell (opposing cylindrical windows are located on the front and back of the vessel) to visually determine if there are two phases present (alkane-rich fluid and the polymer) in the sample volume. If two phases are present, the polymer has not dissolved fully at these conditions. Because then entire contents of the windowed high pressure sample volume can be directly observed,

“dissolution” is ascertained as the attainment of a transparent, stable single phase in which no residue of polymer is visible. This single phase of known composition is then very slowly expanded at constant temperature by slowly withdrawing overburden fluid from the cell with the first PD pump, resulting in a very slow reduction in pressure. This action is continued until the first appearance of a second phase composed of small droplets or particles of polymer, is observed (Fig. 1e). Because the polymer particles appear throughout the sample volume and render it opaque, this condition is commonly referred to as a cloud point. The cloud point pressure, which represents the lowest equilibrium pressure required for the polymer and NGL component (and hexane, if present) to form a single phase, can be determined various temperatures and pressures. Cloud point pressures are repeated at each test condition (constant temperature and overall composition) 5 times. The error associated with the measurement of cloud point data for polydisperse polymers in a high pressure solvent is ± 0.7 MPa.

3.2 Falling ball viscometry test

There are many types of high pressure viscometers and rheometers (e.g. falling object, rolling ball, sliding cylinder, vibrating crystal, vibrating wire, capillary, Couette) that are useful for measuring the viscosity of supercritical fluids or compressed liquids. These are reliable tools when one has no doubt that a single phase exists within the high pressure sample volume. However, it is advantageous to employ a fully windowed viscometer (i.e. one that allows observation of the entire contents of the sample volume) for studies of CO₂ or NGL thickeners because these thickeners are often difficult to dissolve and may come out of solution as temperature or pressure conditions change. Even small particles of undissolved thickener or small swollen masses of softened thickener particles can cause dramatically erroneous results. For example, a single particle or piece of soft, undissolved polymer can clog a narrow piece of capillary tubing, resulting in a large pressure drop that gives the illusion of a thickened solution (Zhang et al., 2011). Likewise a particle can inhibit or slow the fall of a ball or cylinder, the roll of a ball, the vibration of a crystal, or the rotation of a surface that is solely positioned

263 to a stationary surface with fluid filling the gap. This type of viscometry was previously used
264 extensively by our own team at the University of Pittsburgh (Enick, 1991; Hong et al., 2008; Kilic et al.,
265 2003; Miller et al., 2009; Xu et al., 2003), Heller and co-workers at New Mexico Institute of Mining and
266 Technology Petroleum Recovery Research Center during their study of CO₂, propane and butane
267 thickeners (Dandge and Heller, 1987), and DeSimone and co-workers at University of North Carolina -
268 Chapel Hill and Oak Ridge National Laboratory during their study of polyfluoroacrylate homopolymer
269 thickeners for CO₂ (McClain et al., 1996). Therefore high pressure, close clearance falling ball
270 viscometry in a high pressure windowed cell phase behavior cell was employed in this study to measure
271 the viscosity of thickened ethane, propane and butane, as illustrated in **Fig. 2**.

272 The procedure for charging the sample volume with polymer and NGL component (and hexane, if
273 present) is identical to the procedure for phase behavior, except that a Pyrex ball is also inserted into the
274 sample volume of the Pyrex tube. The mass of polymer and NGL component are chosen to require a
275 relatively large volume of solution (90-100 ml) at the designated temperature and pressure in order to
276 give the Pyrex ball the longest possible column of liquid to fall through. A transparent single phase
277 solution at a pressure above the cloud point pressure of the mixture composition is then established in
278 the sample volume of a thick-walled Pyrex tube (3.175 cm inside diameter). Initially, the Pyrex ball
279 (2.23 g/cm³, 3.1587 cm diameter) rests on the sliding piston at the bottom of the sample volume. The
280 entire high pressure cell, which is mounted on a small platform that can be rotated, is then rapidly
281 inverted and the ball is permitted to fall through the entire 14 cm vertical column of the high pressure
282 sample. It is easy to visually detect the occurrence of any undissolved thickener that can alter the
283 uniform fall of the sphere. Velocity measurements taken at various positions along the fall are used to
284 verify that the terminal velocity has been attained, which typically occurs after the ball has fallen one-
285 third of the height of the sample volume. The terminal velocity of the falling ball was therefore
286 measured as the time required for the ball to fall 2 cm at a position at the midpoint of the sample

287 volume. Terminal velocity measurements are repeated 10 times, and in all cases these 10 readings are
 288 within $\pm 10\%$ of the average terminal velocity. The terminal velocity of the ball falling through the
 289 thickened alkane was then compared to the terminal velocity of the ball falling through the pure alkane
 290 at the same temperature and pressure in order to determine how effective the polymer was in thickening
 291 the fluid.

Fig. 2. Close clearance high pressure falling ball viscometer operation

294 4. Calculations

295 The governing equation for a falling ball viscometer can be used to estimate the degree of viscosity
 296 enhancement associated with a thickener. For a falling ball viscometer,

$$\mu = K \frac{(\rho_{ball} - \rho_{fluid})}{V_t} \quad (1)$$

297 where K is the viscometer constant that is dependent upon the ball and tube diameter (Huang et al.,
 298 2000; Xu et al., 2003) and is typically determined via calibration with a fluid of known density and

viscosity over a range of temperature and pressure, such as pure propane. ρ_{ball} and ρ_{fluid} are density values of ball and fluid, respectively, and V_t is terminal velocity of the falling ball. For example, at 25°C and 13.79 MPa (2000 psi), the calibration constant is 0.064 mPa cm⁴. Examples of the method used to determine the calibration constant of this viscometer are provided in the Appendix. However we are primarily interested in the change in viscosity induced by the polymer, which is the ratio of the viscosity of the fluid with a dissolved thickener to the viscosity of the pure fluid, $\frac{\mu_{\text{sol}}}{\mu_o}$. This ratio is referred to as the relative viscosity. If one assumes that the dilute concentration of polymer does not significantly affect fluid density, then Equation 1 can be used for the thickened alkane and the pure alkane at the same temperature and pressure, and the ratio of these expressions yields the relative viscosity of the thickened solution,

$$\text{Relative Viscosity} = \frac{\mu_{\text{sol}}}{\mu_o} = \frac{V_{t\text{sol}}}{V_t} \quad (2)$$

Where, μ_{sol} is viscosity of solution containing a specified amount of thickener in a specific alkane, μ_o is viscosity of the pure alkane, V_t is terminal velocity of ball in the pure fluid and $V_{t\text{sol}}$ is terminal velocity of ball in solution with polymer. Therefore the viscometer constant is not required for the determination of relative viscosity. All thickening results are reported as a function of relative viscosity and the error bar over data points in all of the relative viscosity plots reflect the range of relative viscosity based on 10 measurements of the terminal velocity values associated with each set of conditions.

Because the sample volume that retains the fluid and the ball is closed, the displaced fluid flows up and around the falling ball (unlike other versions of close clearance high pressure falling ball viscometers in which the tube is vented at top and bottom and open to a pool of the fluid (Calvignac et al., 2010)). To the best of our knowledge, there is only a single publication that presents an expression for the average shear rate on the surface of a close clearance ball falling at its terminal velocity in a column of a Newtonian fluid retained in a tube with a slightly larger diameter than the ball, that by Doffin et al.

321 (Doffin et al., 1984). These researchers stated that the maximum shear rate on the surface of the sphere
 322 occurs at the position along the equatorial plane where the gap between the ball and sphere is smallest.
 323 They expressed this maximum shear rate γ as

$$\gamma_{max} = \left(\frac{V_t (3R^2 + r^2 + 2Rr)}{(R + r)e^2} \right) \quad (3)$$

324 Where V_t is terminal settling velocity of the ball, R is the inside radius of the tube, r is the radius of the
 325 ball, and e is the smallest gap between the ball and the tube ($R-r$). The authors then stated that the
 326 average shear rate on the falling ball, γ_{avg} , was equal to one half of the maximum value

$$\gamma_{avg} = 0.5 \left(\frac{V_t (3R^2 + r^2 + 2Rr)}{(R + r)e^2} \right) \quad (4)$$

327 However, this paper provided neither a derivation nor citation demonstrating that the average shear rate
 328 is actually equal to half of the maximum shear rate. Nonetheless, these expressions have been used by
 329 others to estimate the average shear rate on the falling ball, although Fons and co-workers mistakenly set
 330 the parameter “ e ” equal to the difference in tube and ball diameters rather than radii (Fons et al., 1993).
 331 In this work we equate the maximum shear rate at the position of the smallest gap to the analytic
 332 solution for the shear rate at the wall of a falling cylinder (with the same radius as the ball) that falls
 333 through a Newtonian fluid at the same velocity as the ball (Barrage, 1987; Heller and Taber, 1982;
 334 Huang et al., 2000).

$$\gamma_{max} = V_t \left(\frac{-2r - (R^2 - r^2) \frac{1}{r \ln\left(\frac{r}{R}\right)}}{\ln\left(\frac{r}{R}\right) (r^2 + R^2) + (R^2 - r^2)} + \frac{1}{r \ln\left(\frac{r}{R}\right)} \right) \quad (5)$$

335 Equation 5 is valid for any value of r/R . Equation 3 is an excellent approximation for equation 5 only
 336 for values of $r/R > 0.95$. As values of r/R become increasingly smaller, the deviation between equation
 337 3 and 5 becomes increasingly significant.

338 Rather than arbitrarily setting the average shear rate equal to one-half of the maximum value, we
339 determine a surface-area averaged value. This derivation is provided in the Appendix. The final
340 expression for the average shear rate associated with the ball and tube radii of the viscometer used in this
341 work is

$$\gamma_{avg}(s^{-1}) = 7,120 V_t \left(\frac{cm}{s} \right) \quad (6)$$

342 This result indicates that the average shear rate for our viscometer is about 10% of the maximum shear
343 rate, rather than the 50% value suggested by Doffin et al. (Doffin et al., 1984). The procedure provided
344 in the Appendix can be used to determine the value of the constant in equation 6 for falling ball
345 viscometers with other values of r and R .

346 As detailed in the Appendix, the terminal viscosity of the Pyrex ball falling through the pure NGL
347 components at the temperatures and pressures of interest was approximately 1 cm/s at 25°C. Therefore
348 the average shear rate can be estimated using equation 7.

$$\gamma_{avg}(s^{-1}) \approx \frac{7,120}{Relative\ Viscosity} \quad (7)$$

349 Equation 5 provides an accurate value for the maximum shear rate at 25°C, while equation 6 provides an
350 estimate of the surface area-average shear rate at 25°C experienced on the surface of a ball falling
351 through a closed tube with a Newtonian fluid. These equations also provide reasonable estimates for the
352 maximum and average shear rate for the experiments conducted at 40°C and 60°C.

353 **5. Results and Discussion**

354 High pressure solutions were prepared with DRA, PIB, and PDMS.

355 **5.1 PIB results**

356 PIB is insoluble in high pressure ethane, propane and butane; there are no signs of polymer swelling or
357 dissolution after 6 hours of mixing at 25-80°C. Even when a transparent solution of 1wt% PIB in
358 hexane is first prepared by slowly stirring a mixture of PIB and hexane for 24 hours and then

introducing the NGL component, the PIB immediately precipitates when the high pressure light alkane is added to the mixture and the PIB remains undissolved after prolonged mixing at high pressure.

5.2 PDMS results

PDMS dissolves readily at concentrations up to at least 2wt% (higher concentrations were not assessed) in ethane, propane and butane at pressures above the cloud point pressure values listed in **Table 1**. PDMS was soluble at pressures slightly above the vapor pressure of propane and butane. In ethane, however, pressures much greater than the vapor pressure are required for dissolution. The vapor pressures of these light alkanes are provided in **Table 2**. The high solubility of lower molecular weight samples of PDMS in NGL constituents has been previously attributed to the high thermal expansion coefficient for PDMS (Zeman et al., 1972), which exhibits LCST (Lower Critical Solution Temperature) behavior in various fluids. LCST behavior refers to the fact that as the temperature increases one needs higher pressures to dissolve the polymer in a solution; most polymers exhibit this trend in highly compressible fluids. This behavior is generally thought to be entropically driven because as the free volume of the solvent and polymer become significantly different, the system phase splits so that the solvent-rich phase can maximize its entropy. As such, the key variable is the coefficient of thermal expansion of each of the components; PDMS has a very high expansion coefficient and hence it will maintain a single phase with very compressible fluids long after others have phase split. Further, the miscibility of PDMS with the light alkanes is consistent with their respective solubility parameter values. PDMS has a solubility parameter in the 14.9-15.5 MPa^{0.5} range and for liquid ethane, liquid propane and liquid *n*-butane the solubility parameter values are 11.7, 13.4 and 14.1 MPa^{0.5}, respectively, as estimated with a group contribution method (Hansen, 2007). The difference between the solubility parameter values of PDMS and the liquid alkanes (*n*-butane and propane) differ by less than 2.05 MPa^{0.5}, which is consistent with the high degree of solubility in these alkanes. The difference between

the solubility parameter values of PDMS and ethane is greater than 2.05 MPa^{0.5}, however. Therefore it is not surprising that extremely high pressures were required for the PDMS to dissolve in ethane.

Table 1 Cloud point pressures of PDMS in NGL

Solvent	Concentration	Cloud point (MPa)		
	(wt%)	25°C	40°C	60°C
Ethane	1	11.86	13.51	17.72
	2	12.00	14.00	18.00
Propane	1	1.00	1.55	2.45
	2	1.07	1.63	2.56
n-butane	1	0.28	0.41	0.76
	2	0.31	0.47	0.92

Table 2 Vapor pressure of light alkanes (NIST Chemistry Webbook, 2016)

Solvent	Vapor Pressure in (MPa)		
	25°C	40°C	60°C
Ethane	4.19	Supercritical	Supercritical
Propane	0.95	1.37	2.12
n-Butane	0.24	0.38	0.64

The relative viscosity (viscosity of the solution/viscosity of the pure alkane at the same temperature and pressure) of high pressure ethane, propane and butane-rich solutions containing 1wt% or 2wt% PDMS is illustrated in **Figs. 3, 4 and 5**, respectively. Despite its high molecular weight and ability to dissolve in ethane, PDMS is ineffective at thickening ethane; hardly any increase is observed at 1wt% and only a 20% increase is observed at 2wt% PDMS and 62.05 MPa (9000 psi) at 25°C. PDMS was more effective

394 in thickening propane. For example, at a concentration of 2wt% PDMS the propane-rich solution was
 395 twice as viscous as pure propane at 62.05 MPa. The greatest thickening effect at a specified mass
 396 concentration is achieved in butane, where a 4-fold increase in butane viscosity is realized at 2wt%
 397 PDMS and 62.05 MPa. In all cases, the PDMS polymer is a better thickener at higher pressures. The
 398 average shear rates for these experiments were determined with equation 6 and are provided along with
 399 each figure; the values vary between 1750 s^{-1} to 7100 s^{-1} . Because the PDMS provided so little
 400 thickening of the solution, the Pyrex ball fell quickly and these shear rates were far above those
 401 associated with flow within porous media during EOR.
 402 High molecular weight PDMS does not appear to be a viable thickener for NGL used during EOR.
 403 Although PDMS is soluble in propane and butane at pressures slightly above their vapor pressures,
 404 extremely high pressure is required for dissolution in ethane. More important the degree of viscosity
 405 enhancement is very modest even for butane, which is the NGL component most effectively thickened
 406 by PDMS. For example, the addition of 2 weight percent PDMS to butane at 25°C results in only a
 407 doubling of viscosity.

408 **Fig. 3.** Relative viscosity change in ethane by PDMS at 25°C and average shear rate (Equation 6) of $6000\text{--}7100\text{ s}^{-1}$. Δ 2 wt%
 409 PDMS; $\circ$ 1 wt% PDMS.
 410

Fig. 4. Relative viscosity change in propane by PDMS at 25°C and average shear rate (Equation 6) of 3500-7100 s⁻¹. Δ 2 wt% PDMS; $\circ$ 1 wt% PDMS.

Fig. 5. Relative viscosity change in n-butane by PDMS at 25°C and average shear rate (Equation 6) of 1750-7100 s⁻¹. Δ 2 wt% PDMS; $\circ$ 1 wt% PDMS.

5.3 DRA results

The solubility of the DRA polymer in ethane, propane and butane at 25°C, 40°C and 60°C is represented by the cloud point data found in **Table 3** for solutions containing up to 0.5 wt% DRA polymer. For

concentrations up to and including 0.2 wt% DRA in NGL component, the DRA-1% solution was used to prepare the mixture. Therefore, every high pressure solution contained 99 times as much hexane as the DRA. For example, the 0.04% DRA solution in butane actually was composed of 0.04% DRA polymer, 3.96% hexane, and 96% butane. For concentrations of 0.25wt% and higher DRA polymer in NGL component, the DRA-2% solution was used to prepare the mixture. These high pressure solutions contained 49 times as much hexane as the DRA polymer. For example, the 0.50% DRA polymer solution in butane actually was composed of 0.50% DRA polymer, 24.50% hexane, and 75% butane. The hexane can be considered as a co-solvent for the DRA polymer.

Solubility results are presented in **Table 3**. At dilute concentrations, this polymer is soluble in butane and propane at pressures close to the vapor pressure of butane and propane. In ethane, however, much higher pressures are required to attain solubility. As in the case of PDMS, this reflects that ethane is a substantially weaker solvent for a high molecular weight polymer than propane or butane. Therefore unacceptably high pressure may be required to dissolve this DRA polymer in an ethane-rich NGL.

Table 3 Cloud point pressure of DRA polymer in light alkanes. DRA polymer is part of a 1wt% DRA in 99% hexane solution except for mixtures designated as *, in which case a 2wt% DRA in hexane solution was used.

Solvent	DRA polymer conc.	Hexane conc.	Cloud point (MPa)		
	(wt%)	(wt%)	25°C	40°C	60°C
Ethane	0.01	0.99	35.44	39.78	40.93
	0.04	3.96	34.06	37.40	40.37
	0.10	9.90	29.73	33.16	37.37
	0.20	19.80	21.65	25.23	28.41
	0.25*	12.25	44.33	46.26	47.46
	0.50*	24.50	42.30	44.95	46.95

Propane	0.01	0.99	1.00	1.55	2.45
	0.04	3.96	0.99	1.54	2.40
	0.10	9.90	0.98	1.54	2.38
	0.20	19.80	0.97	1.52	2.34
	0.25*	12.25	1.43	2.31	2.99
	0.50*	24.50	1.45	2.17	3.07
Butane	0.01	0.99	0.26	0.41	0.66
	0.04	3.96	0.26	0.41	0.66
	0.10	9.90	0.26	0.41	0.64
	0.20	19.80	0.26	0.41	0.63
	0.25*	12.25	0.29	0.43	0.71
	0.50*	24.50	0.29	0.44	0.77

436

437 The increases in viscosity attained with dilute concentrations of DRA polymer (along with hexane as a
438 co-solvent) are presented in **Figs. 6-14**. As was the case for the PDMS polymer, in all cases the relative
439 viscosity of the poly- α -olefin solutions increase with increasing pressure. Further, the viscosity increases
440 attained in ethane and propane are comparable and significantly less than those realized in butane. For
441 example, a 0.25wt% DRA polymer concentration is required to roughly double the viscosity of ethane
442 and propane, **Figs. 6-11**, while only 0.10wt% DRA polymer is required to double the butane viscosity,
443 **Figs. 12-14**. At 0.50wt% DRA polymer, 3-9-fold increases in ethane and propane viscosity occur, while
444 23-30 fold increases occur in butane at a 0.50wt% DRA polymer concentration.

445 Although we do not have direct experimental confirmation of increased swelling of dissolved polymer
446 coils resulting in increased viscosity, these effects are consistent with classical polymer-solvent viscosity
447 theory (Flory and Fox, 1996). Alkane solvent strength increases with pressure and with an increasing
448 carbon chain length, as reflected by increases in solubility parameter with both increasing pressure and

increasing carbon number (Hansen, 2007). As the solvent shows increasing thermodynamic affinity for the polymer, it expands the polymer coils in solution, eventually causing an overlap between polymer chains and hence higher viscosities (Fried, 2014). Therefore it is possible that our results reflect that stronger solvents, such as high pressure butane, not only dissolves the polymer but also because the dissolved polymer molecules to swell and overlap to a greater extent than they do in poorer solvents, such as low pressure ethane.

These results indicate that butane is a significantly stronger solvent for the dissolution and swelling of ultrahigh molecular weight polymers than ethane or propane.

The average shear rates for these experiments were determined with equation 6 and are provided along with each figure; the values vary between 400 s^{-1} for the highest viscosity fluid to 7100 s^{-1} for the lowest viscosity fluid.

Fig. 6. Relative viscosity change by DRA in ethane at 25°C and average shear rate (Equation 6) of 1500-7100 s^{-1} . - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; Δ 0.01 wt%.

Fig. 7. Relative viscosity change by DRA in ethane at 40°C and average shear rate (Equation 6) of 1500-7100 s⁻¹. - 0.50 wt%;
x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 8. Relative viscosity change by DRA in ethane at 60°C and average shear rate (Equation 6) of 800-7100 s⁻¹. - 0.50 wt%;
x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 9. Relative viscosity change by DRA in propane at 25°C and average shear rate (Equation 6) of 1000-7100 s⁻¹. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 10. Relative viscosity change by DRA in propane at 40°C and average shear rate (Equation 6) of 1200-7100 s⁻¹. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 11. Relative viscosity change by DRA in propane at 60°C and average shear rate (Equation 6) of 800-7100 s⁻¹. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 12. Relative viscosity change by DRA in butane at 25°C and average shear rate (Equation 6) of 400-7100 s⁻¹. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; △ 0.01 wt%.

Fig. 1. Relative viscosity change by DRA in butane at 40°C and average shear rate (Equation 6) of $\sim 400\text{--}7100\text{ s}^{-1}$. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; Δ 0.01 wt%.

Fig. 24. Relative viscosity change by DRA in butane at 60°C and average shear rate (Equation 6) of $\sim 400\text{--}7100\text{ s}^{-1}$. - 0.50 wt%; x 0.25 wt%; □ 0.20 wt%; ◇ 0.10 wt%; ○ 0.04 wt%; Δ 0.01 wt%.

The DRA viscosity enhancement results of **Figs. 6 – 14** are much more promising than those associated with either PIB or PDMS. Therefore it is recommended that future research studies focus solely on ultra-high molecular weight NGL-soluble polymers, especially for butane, propane, and butane-propane

491 mixtures that are likely to dissolve the polymer at relatively low pressure. However, the field-scale use
492 of DRA at this point in the form of DRA-1% and DRA-2% solution in hexane would be advised.
493 Consider that these results shown in **Figs. 6 – 14** indicate that increasing the viscosity of NGL
494 components by roughly an order-of-magnitude with ultra-high molecular weight DRA polymer will
495 require polymer concentrations of about 5,000 ppm. Because the DRA polymer is available as 2%
496 solution in hexane (DRA-2%), a field operator seeking to attain an order of magnitude increase in NGL
497 viscosity would need to inject roughly one-third as much DRA-2% solution as NGL to form a 25%
498 (DRA-2% solution) and 75% NGL. This is an imposing amount of extremely viscous solution to be
499 brought into the oilfield operation and pumped into the pipe carrying NGL. Further, rapid dissolution of
500 the DRA in the NGL would require that as one pumps the solution of DRA polymer in hexane into the
501 NGL line on the surface into a section of pipe with static mixers immediately downstream of the DRA
502 solution injection port, the pressure at the point of the DRA solution introduction would be above the
503 cloud point pressure of the overall mixture at the surface temperature. For example, **Table 3** shows that
504 the dissolution of 5000 ppm DRA (added in the form of DRA-2%) in propane at 40°C requires a
505 reasonable pressure of only 2.17 MPa, but **Fig. 10** indicates that a relatively low 3-fold increase in
506 viscosity would be attained. However, an unreasonably high pressure of 55 MPa would be required for
507 6-fold viscosity increase. The results in **Table 3** also make it clear that it would be difficult to dissolve
508 the DRA polymer (even with the hexane co-solvent) in an ethane-rich NGL at pressures even close to
509 typical reservoir conditions. For example, the dissolution of 5000 ppm DRA (added in the form of
510 DRA-2%) in ethane at 40°C requires a pressure of 44.95 MPa. Further, the overall mixture composition
511 would need to remain in the single-phase region (i.e. above the cloud point pressure) along the entire
512 temperature-pressure path taken by the mixture from the point of DRA addition on the surface to the
513 bottom of the injector to the pore space of the formation at the approximate position of the NGL-oil
514 mixing zone.

6. Conclusion

An ultra-high molecular weight poly- α -olefin drag reducing agent (DRA) with an average molecular weight greater than $2.0 \cdot 10^7$, a high molecular weight polyisobutylene (PIB, M_w $1.0 \cdot 10^7$), and a high molecular weight silanol-terminated polydimethyl siloxane (PDMS, M_w $9.8 \cdot 10^5$) were assessed as thickeners for the three main components of NGL, ethane, propane and butane at temperatures of 25°C, 40°C and 60°C, concentrations less than 1wt%, and pressures to 69 MPa. Viscosity was determined with a high pressure falling ball viscometer and, for the first time, an expression for the average shear rate associated with this type of device was derived.

PIB fails to dissolve in these light alkanes even when 100 times as much hexane as PIB is added to the high pressure mixture.

PDMS is soluble in ethane, propane and butane, although much higher pressures are required for dissolution in ethane. For example at 25°C, pressures of 12.00, 1.07 and 0.31 MPa are required to dissolve 2 wt% PDMS in ethane, propane and butane, respectively. In all cases an increase in pressure leads to a slight increase in viscosity. However, the viscosity enhancement is modest even at a very high pressure of 62.05 MPa (3.8-fold for butane, 2.0-fold for propane, and 1.2-fold for ethane). At a specified concentration (wt%) in the high pressure solution, PDMS is most effective as a thickener for butane, and least effective for ethane. These PDMS-induced levels of viscosity enhancement appear to be too modest for silanol-terminated PDMS to be a promising candidate for field application, especially if the NGL is ethane-rich.

The ultra-high molecular weight poly- α -olefin DRA polymer, which is available as a 1% or 2% pre-dissolved solution in hexane, was the most effective thickener for ethane, propane and butane. Dissolution at concentrations up to 0.5wt% (5000 ppm) and temperatures between 25°C and 60°C occurred at relatively low pressure for propane and butane. An increase in pressure leads to a slight increase in the ability of the DRA to thicken the solution. At 0.50wt% of the DRA polymer (and 24.5%

hexane), 3-9-fold increases in ethane and propane viscosity occur, while 23-30 fold increases occur in butane. However, the viability of the poly- α -olefin as a practical NGL thickener during field-scale EOR will be hindered by its possible insolubility in ethane-rich NGL at operating conditions, the large volumes of hexane co-solvent (present in the formulations used in this study) that would also have to be pumped into the NGL along with the polymer, and the possibility of unrealistically high pressures being required to attain the desired level of viscosity enhancement.

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664

665 Appendix

666 Average shear rate determination

667 The calculation used to determine the average shear rate associated with a falling ball viscometer
668 involved modeling the ball as a stack of thin horizontal cylinders of incrementally different diameter
669 that, as an aggregate, closely simulates the shape of the sphere, as illustrated for four cylinders for each
670 hemisphere in **Fig. (a)**. In this manner cylindrical coordinates could be used for both the ball and the
671 cylindrical wall.

672
673 **Fig. (a).** Multiple cylinder approximation of sphere used to derive average shear rate expression based on cylindrical
674 coordinates

675 For this approximation, the results are insensitive to the number of cylinders if at least 2000 cylinders
676 are used. If it is assumed that the volumetric flow rate of the fluid displaced by the falling ball, Q ,
677 remains invariant for each of the annular spaces associated with the 4000 cylinders, then:

$$Q = \pi r^2 V_t \quad (i)$$

678 The shear rate along the vertical wall of each cylinder can therefore be determined using equation 5,
679 with r corresponding to the radius of the thin cylinder (r_c) and with V_t set equal to the velocity of the
680 cylinder required to attain the volumetric flow rate in the annular gap, V_{tc} .

$$V_{tc} = Q / \pi r_c^2 \quad (ii)$$

681 To obtain a surface area-average shear rate, the products of the shear rate and the surface area of the
682 short vertical wall of each for each cylinder are summed. This summation is then divided by the total

area of the vertical walls of the cylinders. These calculations were repeated for numerous examples with ratios of $0.95 < r/R < 0.9999$, and in each case the surface area-averaged shear rate was compared to the maximum shear rate. The results are expressed in the following equation;

$$\frac{\gamma_{avg}}{\gamma_{max}} = -4.354 \times 10^8 \left(\frac{r}{R}\right)^6 + 2.540 \times 10^9 \left(\frac{r}{R}\right)^5 - 6.175 \times 10^9 \left(\frac{r}{R}\right)^4 + 8.005 \times 10^9 \left(\frac{r}{R}\right)^3 - 5.837 \times 10^9 \left(\frac{r}{R}\right)^2 + 2.270 \times 10^9 \left(\frac{r}{R}\right) - 3.678 \times 10^8 \quad (iii)$$

This result is dominated by the portion of the sphere surface near the gap, where the shear rates are the highest and the surface areas of the thin cylinders are the greatest.

A very similar result for the ratio of the average shear rate to the maximum shear rate is obtained for the surface area average shear rate of a close clearance falling ball viscometer if the terminal velocity of each thin falling cylinder is maintained at a single value; the terminal velocity of the ball.

$$\frac{\gamma_{avg}}{\gamma_{max}} = -4.372 \times 10^8 \left(\frac{r}{R}\right)^6 + 2.551 \times 10^9 \left(\frac{r}{R}\right)^5 - 6.200 \times 10^9 \left(\frac{r}{R}\right)^4 + 8.038 \times 10^9 \left(\frac{r}{R}\right)^3 - 5.861 \times 10^9 \left(\frac{r}{R}\right)^2 + 2.279 \times 10^9 \left(\frac{r}{R}\right) - 3.693 \times 10^8 \quad (iv)$$

The maximum shear rate at the ball surface occurs in the smallest gap position between the ball and tube, and either equation 3 or 5, for $R = 1.58750 \times 10^{-2}$ m and $r = 1.57935 \times 10^{-2}$ m, gives a maximum shear rate of

$$\gamma_{max}(s^{-1}) = 71,700 V_t \left(\frac{cm}{s}\right) \quad (v)$$

Based on Equations 5 and (iii) from this work, the surface area-average shear rate (based on the assumption that the volumetric flow rate in the horizontal annuli between the falling ball and tube remains constant for each of the cylinders) is

$$\gamma_{avg}(s^{-1}) = 0.09934 (71,700) V_t \left(\frac{cm}{s}\right) = 7,120 V_t \left(\frac{cm}{s}\right) \quad (vi)$$

697 Similarly, based on Equations 5 and (iv) from this work, the surface area-average shear rate (assuming
 698 that the terminal velocity of each of the cylinders is the same as the terminal velocity of the sphere) is

$$\gamma_{avg}(s^{-1}) = 0.09828 (71,700) V_t \left(\frac{cm}{s} \right) = 7,050 V_t \left(\frac{cm}{s} \right) \quad (vii)$$

699 These results are very similar and indicate that the average shear rate for our viscometer is about 10% of
 700 the maximum shear rate, rather than the 50% value suggested by Doffin et al. (Doffin et al., 1984).

701 When the viscometer was calibrated at 25°C with pure ethane, propane and butane the terminal velocity
 702 varied between 1.03 – 1.11, 0.91 – 0.95, and 0.81 – 0.89 cm/s for ethane, propane and butane,
 703 respectively. This corresponds to average shear rates of 7330 – 7900, 6480 – 6760, and 5770 – 6340 s⁻¹
 704 for the Pyrex ball falling through pure ethane, propane and butane at the conditions associated with this
 705 study.

706 If one desires to obtain a single expression that provides a reasonable estimate of the shear rates reported
 707 in the results for 25°C, one can use a falling ball terminal velocity for pure alkanes of roughly 1 cm/ in
 708 equation (vi), which allows the average shear rate of the ball falling through the pure NGL component,
 709 equation (vi), to be estimated as

$$\gamma_{avg} \approx 7120 s^{-1} \quad (viii)$$

710 Because the terminal velocity of the ball falling through the polymer-NGL solution is smaller than the
 711 terminal velocity of the ball falling through the pure NGL by the factor of relative viscosity increased as
 712 reported in equation 2.

$$V_{tsol} = \frac{V_t}{Relative\ Viscosity} \quad (ix)$$

713 Therefore one can combine equations (vi) and (ix) to obtain average shear rate expression in polymer-
 714 NGL solution at 25°C as

$$\gamma_{avg}(s^{-1}) \approx \frac{7,120}{Relative\ Viscosity} \quad (x)$$

Equation (x) serves only as a rough estimate of the average shear rate for temperatures greater than 25°C because precise measurements of the Pyrex ball diameter or the Pyrex tube diameter, which are required for **equations (i) – (vii)** and for the determination of the constant found in **equations (viii) and (x)**, are not available at high temperature and pressure.

It is important to note that neither the maximum shear rate nor the average shear can be pre-selected; the shear rate is actually a dependent variable in these tests. Both of these shear rates are functions of the terminal velocity of the sphere and the radii of the ball and tube. Further, the terminal velocity is also a function of the density difference between the sphere and the fluid. Therefore the only way to obtain viscosity data as a function of average shear rate is to drop balls of varying size and density through the same fluid. Nonetheless, the foremost utility of employing a single Pyrex ball (as was done in this work) is that it enables the direct comparison of various polymers in NGL components at the same polymer concentration, temperature and pressure. An effective thickener will result in a slow fall of the ball, which corresponds to high relative viscosity values at low shear rates. An ineffective thickener will result in the ball falling quickly yielding low relative viscosity at high shear rates.

For the conditions of this study, shear rates as low as $\sim 400 \text{ s}^{-1}$ were attained for the most effective thickeners. These average shear rate ranges are higher than the $1\text{-}5 \text{ s}^{-1}$ range in the vast majority of the reservoir and near wellbore values of up to 100 s^{-1} . Therefore the polymer solutions reported in this study may exhibit somewhat higher viscosity values at lower shear rates than reported in this work if these dilute solutions are shear-thinning. The pure alkanes used in this study are Newtonian, however the dilute polymer solutions prepared in this study are likely to be non-Newtonian, shear thinning solutions. Therefore these equations for shear rate should be viewed as a means of estimating an approximate maximum and average shear rate associated with the close-clearance falling ball viscometer filled with a dilute polymeric solution.

739 Example of calibration constant determination

740 The calibration constant of a falling ball viscometer, K , is a function solely of the ball diameter and tube
741 inside diameter. For a falling ball viscometer,

$$\mu = K \frac{(\rho_{ball} - \rho_{fluid})}{V_t} \quad (xi)$$

742 Changes in temperature can affect these dimensions slightly, which impacts the calibration constant K .
743 The ball and tube were therefore designed to be composed of the same material, Pyrex 7740, to
744 minimize temperature dependence of K . An increase in pressure can also affect the calibration constant,
745 due to small decreases in the ball diameter with increasing pressure. Because there is no pressure drop
746 across the wall of the tube, changing pressure will not affect the tube inside diameter. One can solve for
747 K by re-arranging Equation (xi)

$$K = \frac{\mu V_t}{(\rho_{ball} - \rho_{fluid})} \quad (xii)$$

748 If one selects a fluid of known density and viscosity at a specified temperature and pressure, the
749 calibration constant can be determined. For example, if one selects propane at 25°C and 2000 psi, the
750 ball density is 2.23 g/cm³, propane density is 0.522 g/cm³ (NIST Chemistry Webbook, 2016), propane
751 viscosity is 0.12 mPa s (NIST Chemistry Webbook, 2016), the experimentally determined terminal
752 velocity is 0.915 cm/s, and the calibration constant is 0.064 mPa cm⁴. This process can be repeated
753 over a range of pressures and temperatures to generate a family of calibration isotherms shown in **Fig.**
754 **(b)**.

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756

757 **Fig. (b).** Calibration constant (K) vs Pressure at 25, 40, 60°C based on calibration with propane

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