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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 0.5 wt% 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 0.2 wt% 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 is introduced as a solution in hexane.

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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

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

Hydrocarbon miscible EOR is not as pervasive in the United States as CO₂ EOR because most of the CO₂ is obtained from massive natural deposits and is transported through extensive CO₂

distribution pipelines, whereas the NGLs used for EOR originate in gas processing plants associated with oil recovery projects (including CO₂ EOR). NGLs are more expensive than CO₂ and this impacts the operating costs and economic viability of the hydrocarbon miscible displacement process. Further, there are markets for NGLs other than for its implementations as an oil recovery solvent; it may be sold for its fuel value (e.g. LPG blends of propane and butane) or for the use as a raw material in the manufacture of chemicals (e.g. cracking ethane to make ethylene). Nonetheless, when there are no nearby markets for NGLs, it can be economical to use NGLs for hydrocarbon miscible EOR. CO₂ miscible and immiscible displacement processes leave substantial amounts of CO₂ behind in the formation, which serves to sequester CO₂. This geologic sequestration will become an increasingly important mode of CO₂ disposal as anthropogenic sources of CO₂ used for EOR become a more significant fraction of the CO₂ supply. However, the NGL left behind in the formation serves solely as an economic loss of solvent.

Although the solvent strength of an NGL mixture is exemplary even at relatively low pressures in shallow reservoirs, this fluid has the same two fundamental disadvantages as CO₂; low density and viscosity relative to crude oil. The density of CO₂ at MMP ranges from roughly 500–700 kg/m³ (Enick et al., 1988; Holm and Jøsendal, 1982). The density of high pressure NGL at typical hydrocarbon miscible conditions is roughly 500 kg/m³. At EOR conditions (i.e. T=20–80 °C, P=2.5–14.0 MPa) 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 injection 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 and 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 increasingly 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 M_w (weight-average molecular weight) 1.08 10⁵ in ethane (Ehrlich and Kurpen, 1963), polyethylene M_w 3.4 10⁵ in propane (Meilchen et al., 1991), polyethylene M_w 4.2 10⁵ in butane (Xiong and Kiran, 1994); poly(ethylene-co-methyl acrylate) M_w 1.0 10⁵ in ethane (Hasch et al., 1992), poly(ethylene-co-methyl acrylate) M_w 1.4 10⁵ in propane and butane (Pratt et al., 1993); poly(ethylene-co-octene) M_w 2.0 10⁵ in propane (Whaley et al., 1997); polypropylene M_w 2.1 10⁵ in propane (Chen et al., 1995); and poly(ethylene-co-acrylic acid) M_w 1.0 10⁵ in propane and butane (Lee et al., 1994). With regard to the highest molecular weight polymers, polyisobutylene M_v (viscosity average molecular weight) 1.66 10⁶ is slightly soluble in compressed liquid butane, but is insoluble in propane and ethane (Zeman et al., 1972). A trimethyl silyl-terminated polydimethyl siloxane M_v 6.26 10⁵ 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. However, there are a few reports of propane and butane being thickened with polymers. For example, in the late 1960s, 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, M_w 1.3 10⁵) 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 0.25 wt% 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 (Ultra-high molecular weight polyacrylamide is water-soluble but NGL-insoluble, therefore it was not considered). DRA polymers typically have ultra-high molecular weights greater than 1.0 10⁷ 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

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