Small associative molecule thickeners for ethane, propane and butane

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Abstract

The abilities of three classes of low molecular weight, metal-based, associative compounds to thicken high pressure ethane, propane or butane have been assessed with a close clearance falling ball viscometer. Tributyltin fluoride (TBTF) does not require a heating/cooling cycle to attain dissolution, and at a concentration of 1wt% in ethane, propane or butane yields 70 - 100-fold viscosity increases at 25°C. Increasing temperature substantially reduces TBTF's thickening ability. Although hydroxyaluminum di-2-ethylhexanoate (HAD2EH) is insoluble in ethane, it does dissolve in liquid propane or butane after mixing at ~100°C and cooling to temperatures as low as 40°C. HAD2EH induces small viscosity increases in propane, but is a very effective butane thickener. Increasing temperature causes a relatively small decrease in HAD2EH's thickening performance. Combining a phosphate ester and a crosslinker in ethane, propane or

butane yields a translucent liquid with viscosity increases that are significantly less than those attained with TBTF or HAD2EH.

Keywords: Ethane, propane, butane, small molecule thickener, association, viscosity

1. Introduction

According to a recent survey published by the Oil & Gas Journal in 2014 [1], hydrocarbon miscible enhanced oil recovery (EOR) has contributed about 1.5% of overall oil production in the US over the past several decades. Hydrocarbon miscible flooding typically involves the injection of natural gas liquids (NGL) [2], a mixture composed primarily of ethane, propane, butane and a small amount of heavier alkanes. This NGL mixture is an excellent solvent for the displacement of oil because it usually exhibits first contact miscibility (i.e. complete miscibility) with crude oil.

Hydrocarbon miscible EOR is not as pervasive in the United States as CO₂ EOR because most of the CO₂ employed is conveniently obtained from massive natural deposits and is transported through an existing CO₂ distribution pipeline network, whereas the NGLs used for EOR originate in gas processing plants associated with oil recovery projects (including CO₂ EOR). Further, there are clearly markets for NGL other than use 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 NGL, it can be economic to use these stranded fluids for hydrocarbon miscible EOR. It is also possible to employ blends of NGL with CO₂ or methane for EOR, especially because larger supplies of CO₂ or methane may be readily available and significantly less expensive than the NGL themselves. CO₂ is a less miscible with crude oil than NGL while

methane is a very poor oil solvent, therefore the addition of these gases to NGL can lead to higher miscibility pressures or an immiscible gas displacement process.

Although the solvent strength of NGL for crude oil is exemplary, they have the same two fundamental disadvantages as CO₂; low density and viscosity relative to crude oil. At hydrocarbon miscible EOR conditions (i.e. T = 25 - 120°C and P = 3 - 20 MPa) ethane, propane and butane exhibit density values of roughly 0.4 g/cm³, 0.5 g/cm³ and 0.6 g/cm³ respectively [1, 3–5]. Because NGL densities are lower than that of crude oil, NGL will exhibit gravity override as they flow through the formation, reducing oil recovery in the lower portions of reservoir. Unfortunately, it is currently not possible to substantially increase the density of NGL with a dilute concentration of an additive.

The viscosity of NGL at reservoir conditions is roughly 0.1 mPa s, significantly lower than that of brine and oil. The range of crude oil viscosity values associated with hydrocarbon miscible projects in the US is 1 – 140 mPa s (1 mPa s = 1 cP), while in Canada crude oil viscosity values in hydrocarbon miscible projects range between 0.1 – 0.8 mPa s [1]. The low viscosity of NGL relative to the crude oil being displaced leads to an unfavorable mobility ratio which, in turn, results in viscous fingering, poor sweep efficiency, and disappointingly low oil recovery. Further, in stratified formations, the viscosity contrast enhances the flow of NGL into thief zones where little to no oil resides. It is possible to diminish the mobility of dense NGL by reducing their relative permeability via a water-alternating gas (WAG) injection process. The objective of this study, however, is to determine if one can reduce NGL mobility by increasing the viscosity of NGL using dilute concentrations of small associating compounds. To be effective, small molecule NGL thickeners should dissolve completely in these high pressure fluids, preferably forming a transparent, thermodynamically stable, single-phase solution capable of flowing

through porous media. Ideally, dissolution and viscosity enhancement can be attained without the need for a two-step process of high pressure heating (which disrupts intermolecular associations) and cooling (which allows the viscosity-enhancing associating network to be established). If the viscosity of NGL solution can be tailored to match that of the crude oil, dramatic improvements in mobility control could result and the need to implement the WAG process would be eliminated.

There is a second, distinct, petroleum-related technology that could benefit from an NGL thickener. NGL can serve as dry hydraulic fracturing fluid in low permeability formations that contain crude oil and/or natural gas and are water-sensitive (i.e. the use of water for fracking causes the permeability of the faces of the fractured rock to decrease). NGL is an excellent alternative solvent for such formations. However the extremely low viscosities of these high pressure liquids results in relatively small fractures and difficulties in transporting high concentrations of proppant particles (usually sand) into the fracture.

Previous work on use of small-molecule thickeners for NGL have focused on trialkyltin fluorides, hydroxy-aluminum surfactants, and mixtures of phosphorous esters and multi-valent metals ions [6–9]. In each case, inter-molecular associations are employed to create non-covalent associations in solution, which then increase viscosity substantially.

1.1 Trialkyltin fluorides

Trialkyltin fluorides typically dissolve in organic liquids after several minutes of stirring. Although heating during the mixing process hastens dissolution, a heating/cooling cycle is not required to attain dissolution of viscosity enhancement.

Tri-n-butyl tin fluoride (TBTF), a white powder with a melting point of 271°C, is an extremely effective thickener for light alkanes. Dunn and Oldfield [10] first reported that TBTF increases the viscosity of non-polar liquid solvents such as n-pentane and carbon tetrachloride. Trialkyltin fluorides are thought to form long linear transient polymeric chains via intermolecular associations between the electropositive tin atom and the electronegative fluorine atom of a neighboring molecule, with the three alkyl chains enhancing solubility in the hydrocarbon solvent and a low enough level of steric hindrance so as to not disrupt the tin-fluorine associations [10], as shown in **Fig. 1**. Heller and co-workers found that TBTF significantly increases the viscosity of high pressure propane and butane [6]. For example, 2-10 fold increases in the viscosity of liquid propane and butane are induced at TBTF concentrations of 0.15 - 0.30 wt% at 25°C and 8.3 MPa (~1200 psi), as determined with a high pressure, close-clearance, falling cylinder viscometer [6]. Enick and co-workers later confirmed that liquid propane and butane could be thickened with TBTF [11]. Heller's group also reported that TBTF was only sparingly soluble in ethane [6] and induced no viscosity change in their sapphire crystal viscometer that was rated to 20.7 MPa (3000 psi) [12].

Other trialkyltin fluorides have also been considered as thickeners for light alkanes. Tripropyltin fluoride is insoluble in hydrocarbon solvents, probably because the C3 arms are too short to promote dissolution in the solvent [13]. Trialkyltin fluorides with longer n-alkyl arms have proven much easier to dissolve, however. Dandge and co-workers found that triamyl-, trihexyl-, trioctyl- and tridecyl-armed tin fluorides were soluble (> 0.4 wt%) in normal alkanes higher than propane as well as in solvents such as cyclopentane and cyclohexane in which tributyltin fluoride was insoluble. However, in a comparison of viscosity change induced in solvents like n-hexane (at 0.1 MPa and 25°C) and n-butane (at 8.3 MPa and 25°C), tributyltin fluoride clearly

outperformed the others at equivalent molar concentrations in the alkane [6]. Apparently, the C4 arms are long enough to enable the compound to dissolve in the light alkane, yet so short that the chain cannot readily bend toward the associating tin and fluoride atoms and disrupt the formation of the linear associating polymer. The longer alkyl arms (C5 – C12) also facilitate dissolution in the light alkanes, but these arms are apparently long and flexible enough to slightly interfere with the associations between the tin and fluorine. For example, at a concentration of 12 mmol l⁻¹ and ambient condition of 1 atm & 25°C, TBTF increased the viscosity of hexane by a factor of 240, while triamyl-, trihexyl-, trioctyl- and tridecyl-armed tin fluorides increased the viscosity by factors of only 100, 150, 120 and 80, respectively.

Fig. 1. Association in trialkyltin fluoride

1.2 Hydroxyaluminum di-2-ethyl hexanoate (HAD2EH)

A mixture of aluminum salts of naphthenic and palmitic acids, (often called “Napalm”), was created during World War II to gel gasoline and hence weaponize this flammable liquid [14–16]. Typically, the mixture of the powdered aluminum disoap and the organic liquid is heated to a temperature high enough to disrupt the intermolecular associations between organo-aluminum molecules (promoting dissolution), and then cooled to allow the disoap molecules to self-assemble into a viscosity-enhancing supramolecular structure, **Fig. 2**. Hydroxyaluminum di-2-ethylhexanoate (HAD2EH), a powder with a melting point of 276°C, is particularly effective in thickening hydrocarbons. HAD2EH was also reported to be effective thickener for compressed liquid propane and butane. At 20°C and HAD2EH concentrations of 0.2-1.0 wt%, 10-100 fold

viscosity increases were detected with a high pressure close-clearance falling cylinder viscometer after many hours of mixing [7]. However, these HAD2EH-propane and HAD2EH-butane solutions were not transparent – instead they were translucent and hazy, indicative that at least a portion of the HAD2EH forms a network of insoluble interlocking fibers in the high pressure liquid propane. Thickened solution composed of liquid propane or butane trapped within a network of interlocking fibers would have great difficulty flowing through sandstone or carbonate rock with pore throat diameters of ~ 1 micron. These fibers would be filtered out of the solution by the surface of the rock into which the mixture was injected.

Fig. 2. Possible association of HAD2EH molecules [17]

1.3 Crosslinked Phosphate Esters (CPE)

Companies such as Halliburton, Ethox Chemicals, and Clearwater Inc. have patented techniques for “gelling” light alkanes with phosphorous-based esters (**Fig. 3**), that are crosslinked with polyvalent metal ions [8, 9, 18–21]. Phosphate (mono, di or the mixture of mono & di) esters with alkyl tails are used commonly. The main application of these gels, which are typically formed with several weight percent of phosphate esters and crosslinking agents, is for dry

hydraulic fracturing. In this work, the use of these compounds to thicken NGL at lower concentrations will be examined for possible EOR application.

Fig. 3. Phosphate di-ester, Phosphate mono-ester, Phosphonic acid ester and Dialkyl phosphinic acid. Commonly used R and R' group identities have been provided.

Typically, two low viscosity liquid reactants, the phosphate ester and a solution containing the dissolved organometallic compound, are added to the liquid that is targeted for thickening. If the polyvalent metal ion can be bound more tightly by the phosphate ester than the ligand that it was originally formulated with in the crosslinker solution, then the phosphate esters will rapidly chelate the metal ions without the need for a heating/cooling cycle and form a linear, supramolecular, micellar structure (**Fig. 4**). If this extended associative structure remains soluble in the liquid, it can quickly and dramatically enhance viscosity. The ease of pumping the phosphate ester and the crosslinking solution, their fast dissolution in solvents, and the rapid kinetics of viscosity enhancement are particularly attractive attributes for the possible use of these phosphate ester systems for thickening NGL during field-scale EOR projects.

Oil-soluble phosphate mono/di-esters, alkyl phosphonic acid ester or dialkyl phosphinic acids can be crosslinked with polyvalent metal ions such as Fe^{3+} , Al^{3+} , Mg^{2+} , Ti^{4+} and Zn^{2+} to induce significant viscosity changes (2-100 fold) in hydrocarbon liquids such as kerosene and diesel oil

at a combined concentration of 0.2-2.5 wt%. [20–22]. It has also been reported that phosphate ester systems can be used to gel mixtures of CO₂ and hydrocarbon liquids [23, 24].

Fig. 4. Mechanism of chelating complex (phosphate ester with metal ion cross linker) [25–28]

Hydrocarbon fluids have been used for fracturing purposes since the 1970's [29, 30]. More recently there have been reports of gelled LPG used in fracturing applications [31, 32]. There have been numerous reports of “gelled” LPG found in the literature [29–33]. However, due to an apparent desire to protect proprietary compositions and techniques, solubility and viscosity data for gelled LPG is relatively scarce [32, 34].

Although TBTF, HAD2EH and CPE have been reported to be potential thickeners for one or more components of NGL, a thorough comparison of the performance of these components in ethane, propane and butane has not been presented. For example, TBTF is known to thicken propane and butane while exhibiting minimal solubility in ethane, but the solubility of TBTF in ethane at pressures above 20.68 MPa has not been evaluated. HAD2EH has only been assessed in propane at room temperature, but its ability to thicken ethane, propane and butane over any temperature range has not been reported. CPE is known to gel organic liquids at ambient temperature and pressure, but claims that CPEs can gel NGL have not been substantiated by phase behavior and viscosity studies for mixtures of CPEs with ethane, propane or butane.

Therefore, the objective of this study is to assess the abilities of TBTF, HAD2EH and CPE to dissolve in and thicken the three main components of NGL (ethane, propane and butane) in the 25 – 100°C temperature range at pressures to 62.05 MPa.

2. Experimental

2.1 Materials

n-pentane (Reagent grade, 98% purity) was purchased from Sigma Aldrich and used as received for ambient pressure screening tests. Ethane, propane and n-butane were obtained from Matheson with a purity level of 99.99% and used without further purification.

TBTF (93% purity) and HAD2EH (96% purity) were procured from TCI America and BOC Science, respectively, and were used as received.

Six Lubrizol Oilfield Solutions (LZOS) phosphate ester products (HGA 70, HGA 70-C6, HGA 37, HGA 37D, HGA 715LP and HGA 702) and three LZOS crosslinking solutions (HGA 65, HGA 48, and HGA 44) were provided by LZOS and used as received. Specific compositions of these proprietary products were not provided, although the MSDS of HGA 48 indicates that AlCl_3 is present. Each crosslinking solution contains a compound with a polyvalent ion. For example, HGA-65 is an organometallic complex that contains a metal ion with a +3 charge that combines with a phosphate ester-based gelling agent, such as HGA-70, to form stable hydrocarbon gels rapidly. For all 18 combinations of phosphate ester and crosslinker, the LZOS products are designed to be used in equal mass concentrations in order to have the appropriate stoichiometric amounts of phosphate ester and polyvalent crosslinker.

2.2 Ambient pressure viscometry

A rotating-dish-and-cup viscometer (Brookfield DV-II+ Programmable Viscometer, M/97-164-D1000) instrument was used for measuring the viscosity of thickened pentane at atmospheric pressure [35].

2.3 Phase behavior measurement

A windowed, variable-volume view cell was used to conduct non-sampling cloud point pressure measurements of mixtures of each thickener in ethane, propane or butane. The details of this experimental procedure for determining thickener solubility have been presented in detail elsewhere [36–38]. In general, a transparent single phase for a mixture of known overall composition was first attained by mixing the thickener (e.g. TBTF or HAD2EH) and the light alkane at pressures as high as 69 MPa at the temperature of interest. In some cases the mixture was also heated to temperatures up to 100°C in order to disrupt the intermolecular associations between thickener molecules, thereby facilitating dissolution; the mixture was then cooled isobarically to the temperature of interest. In the case of the two-component CPE thickener (phosphate ester + crosslinker), the phosphate ester HGA 70-C6 was placed in a small open glass dish at the bottom of the sample volume, while the crosslinker solution HGA 65 was poured around the glass dish. The alkane was then slowly added to the sample volume. This prevented the phosphate ester and the crosslinker from reacting prior to the HGA 70-C6 being dissolved in the high pressure alkane. The transparent single fluid phase was then very slowly expanded at constant temperature until a cloud point (i.e. the appearance of small particles of the thickener) was observed. The cloud point measurement was repeated three times and the average cloud point reported. Typically the error in measurement of cloud point and temperature is ± 0.7 MPa and $\pm 0.1^\circ\text{C}$, respectively.

2.4 High pressure viscometry

A close-clearance, high pressure, windowed, invertible, falling ball viscometer was employed for obtaining the relative viscosity [35]. In a typical experiment, the transparent single phase solution at a pressure above the cloud point of the solution is established in the Pyrex tube (3.1750 cm inside diameter). A Pyrex ball (2.23 g/cm³, 3.1587 cm diameter) is also present at the bottom of the sample volume. The entire cell is then inverted rapidly and the terminal velocity of ball is measured at the mid-point of its fall by measuring the time required for the ball to fall 2 cm. The terminal velocity is also measured in the neat solvent (ethane, propane or butane). Terminal velocity measurements are repeated 10 times and average terminal velocity is recorded. The relative viscosity is the ratio of the viscosity of the fluid with a dissolved thickener to the viscosity of the pure fluid, $\frac{\mu_{sol}}{\mu_o}$. If one assumes that the dilute concentration of polymer does not significantly affect fluid density, then the relative viscosity as measured with a close-clearance falling object viscometer can be expressed as follows [35, 39 – 41].

$$\text{Relative Viscosity} = \frac{\mu_{sol}}{\mu_o} = \frac{V_t}{V_{sol}} \quad (1)$$

Where, μ_{sol} is the viscosity of solution containing a specified amount of thickener, μ_o is the viscosity of the pure fluid, V_t is the terminal velocity of the ball in the pure fluid and V_{sol} is the terminal velocity of the ball in solution with thickener compound. Our group has used this procedure previously to determine the effectiveness of a polyfluoroacrylate polymer to thicken CO₂ [7, 39, 40]. We have recently shown that for our Pyrex ball of diameter of 3.1587 cm, density of 2.23 g/cm³ and cylinder inner diameter of 3.175 cm, the average shear rate over the surface of the falling ball is [35]

$$\gamma_{avg}(s^{-1}) \approx 7000 V_t \left(\frac{cm}{s} \right) \quad (2)$$

3. Results and discussion

3.1 Thickened pentane

In order to ascertain the approximate concentration range over which significant increases in viscosity could be expected in our high pressure testing of NGL, each of the thickening agents was “screened” by dissolving it in n-pentane. The viscosity of the resultant solutions was determined over the shear rate range of 15-450 s⁻¹ at 23°C and 1 atm; the results at a shear rate of 325 s⁻¹ are presented in **Fig. 5**. Higher mass fractions of each thickener dissolved in the pentane, but the viscosity of the resultant solutions exceeded the limits of the Brookfield viscometer. Note that the viscosity values for the HAD2EH solution correspond to data obtained at 30°C (rather than 23°C) because dissolution of HAD2EH requires heating to ~100°C followed by cooling to temperatures no lower than 30°C; at lower temperatures the HAD2EH precipitates from solution. In case of the CPE, the use of the HGA 70-C6 phosphate ester and the HGA 65 crosslinker was found to be the most effective pairing of the 18 possible combinations of six phosphate esters and three crosslinkers.

In order to put the size of the long, linear transient polymers or micelles formed by these small associating compounds in perspective, the viscosity increase associated with a poly- α -olefin with a molecular weight greater than 20,000,000 is also shown in **Fig. 5** [35, 41]. At these relatively low temperatures, the ranking of the thickeners (starting with the best at a specified wt% concentration) is CPE, DRA, HAD2EH, and TBTF. Further, **Fig. 5** indicates that, in general, 0.1 – 0.4 wt% of these thickeners is required for order-of-magnitude changes in solution viscosity.

Fig. 5. Relative viscosity (viscosity of pentane solution/viscosity of pentane) at 325 s^{-1} . x HGA 70-C6 and HGA 65 at 23°C ; Δ poly(α -olefin) at 23°C ; $\square$ HAD2EH at 30°C ; $\circ$ TBTF at 23°C .

3.2 High pressure ethane, propane and n-butane results

3.2.1 TBTF

TBTF dissolves quickly up to 1 wt% in ethane, propane and n-butane at pressures above the cloud point values listed in **Table 1**. The cloud point pressures required to dissolve TBTF in propane and n-butane are only slightly above the vapor pressure of the respective fluids. Dissolution in ethane, however, requires pressures significantly greater than ethane's vapor pressure. This is not surprising because ethane is generally a weaker solvent for organometallic compounds than propane and butane. This is reflected by the very low value of the solubility parameter for liquid ethane, $11.7 \text{ MPa}^{0.5}$, relative to that of liquid propane, $13.4 \text{ MPa}^{0.5}$, and liquid *n*-butane, $14.1 \text{ MPa}^{0.5}$ [42]. Note that all of the cloud point pressures listed for ethane in **Table 1** exceed 20.68 MPa, which was the pressure limit of the viscometer used by Heller and co-workers when they reported that TBTF was sparingly ethane-soluble [6].

Table 1- Cloud point pressure of TBTF in NGL

Solvent	TBTF concentrations	Cloud point (MPa)				
	(wt%)	25°C	40°C	60°C	80°C	100°C
Ethane	0.20	33.34	35.30	39.96	42.30	44.61
	0.50	38.16	40.78	44.47	46.16	47.68
	0.75	38.92	41.33	44.95	47.02	48.44
	1.00	40.44	42.85	47.23	48.33	50.68
Propane	0.50	1.05	1.59	2.45		
	1.00	1.07	1.64	2.55		
n-Butane	0.50	0.31	0.42	0.77		
	1.00	0.36	0.43	0.79		

284 The relative viscosity of the high pressure solutions of TBTF in ethane, propane and n-butane are
 285 provided in the **Figs. 6-9**. **Fig. 6** presents the thickening results for ethane at 25°C as a function
 286 of TBTF concentration and pressure. The viscosity of the solution increases significantly with
 287 TBTF concentration, with only slight increases in viscosity versus pressure. Similar trends were
 288 observed at temperatures as high as 100°C. The relative viscosity values for solutions of TBTF
 289 in ethane at a single pressure of 62.05 MPa are presented in **Fig. 7** as a function of TBTF
 290 concentration (x-axis) and temperature for several isotherms. Clearly, once TBTF concentration
 291 reaches approximately 0.5%, viscosity begins to increase rapidly with further concentration
 292 increases. **Figs. 6** and **7** constitute the first known report that TBTF can dissolve ethane in and
 293 thicken ethane.

294 As previously noted by Heller and coworkers [6] and Enick and co-workers [11], very large
295 increases in propane and butane viscosity are achieved with TBTF (e.g. 70-100 fold at 25°C).
296 Because the TBTF-induced relative viscosity changes for propane and butane are also only
297 slightly sensitive to changes in pressure, only the relative viscosity values at a pressure of 6.89
298 MPa are presented as a function of temperature and TBTF concentration in **Fig. 8** for propane
299 and **Fig. 9** for butane. As in the case of ethane, viscosity begins to increase rapidly with
300 concentration above 0.5%.

301 There is only a very slight increase in relative viscosity with increasing pressure at any
302 temperature and TBTF concentration. This effect is in contrast to the significant increases in
303 relative viscosity with increasing pressure that are observed when ultrahigh molecular weight
304 polymers are used to thicken light alkanes [35], where increased alkane density and solvent
305 strength promote the swelling of polymer coils. TBTF, on the other hand, is a small molecule
306 that self-assembles into a linear supramolecular structure. As long as the TBTF is fully dissolved,
307 further increases in pressure-induced solvent strength apparently do not have a significant effect
308 on solution viscosity.

309 Increasing temperature above 40°C significantly diminishes the intermolecular associations
310 between the tin and fluorine of adjacent TBTF molecules, resulting in notable decreases in
311 relative viscosity for all of the light alkanes. For example, at 25°C, 1% TBTF in ethane and 62.05
312 MPa produces a relative viscosity of 90. At 40°C, the relative viscosity under similar conditions
313 is 75. At 60°C, 80°C and 100°C, the relative viscosity drops to 20, 6 and 2, respectively.

Fig. 6. Viscosity change in ethane by TBTF at 25°C and average shear rate (Equation 2) of 100-7100 s^{-1} (Logarithmic Y-axis). x TBTF at 1 wt%; Δ TBTF at 0.75 wt%; □ TBTF 0.5 wt%; ○ TBTF 0.2 wt%.

Fig. 7. Increase in ethane viscosity caused by TBTF at $P = 62.05$ MPa and average shear rate (Equation 2) of 100-7100 s^{-1} . Δ TBTF at 25°C; □ TBTF at 40°C; ○ TBTF at 60°C; x TBTF at 80°C; + TBTF at 100°C.

Fig. 8. Increase in propane viscosity caused by TBTF at $P = 6.89$ MPa and average shear rate (Equation 2) of 120-7100 s^{-1} . Δ TBTF at 25°C; $\square$ TBTF at 40°C; $\circ$ TBTF at 60°C.

Fig. 9. Increase in butane viscosity caused by TBTF at $P = 6.89$ MPa and average shear rate (Equation 2) of 90-7100 s^{-1} . Δ TBTF at 25°C; $\square$ TBTF at 40°C; $\circ$ TBTF at 60°C.

3.2.2 Hydroxyaluminum di-2-ethyl hexanoate (HAD2EH) results

HAD2EH is ethane-insoluble at pressures to 69 MPa and temperatures to 100°C. The solubility of the HAD2EH in propane and butane at 25°C, 40°C, 60°C, 80°C and 100°C is provided in **Table 2**. Unlike TBTF, the dissolution of HAD2EH in light alkanes requires heating the high pressure mixture to a temperature of ~ 100°C during mixing, attaining a clear solution, and then cooling the solution to the target temperature. HAD2EH remains in solution down to temperatures of 40°C, but precipitates at 25°C in both propane and butane. These solubility results in propane differ somewhat from the earlier report of Enick [7], who reported that HAD2EH obtained from Eastman Kodak could not dissolve in propane, but HAD2EH received from Pfaltz and Bauer did dissolve in propane after a many hours of mixing at 20°C. It is possible that the Pfaltz and Bauer product may have contained an impurity such as ethylhexanoic acid that enhanced the solubility of HAD2EH in propane.

Table 2 - Cloud point data for solutions of HADEH in propane and butane

HADEH concentrations		Cloud point (MPa)				
	(wt%)	25°C	40°C	60°C	80°C	100°C
Ethane	0.50	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
	1.00	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Propane	0.50	Insoluble	1.59	2.45	3.53	5.38
	1.00	Insoluble	1.64	2.55	3.62	5.62
n-Butane	0.50	Insoluble	0.42	0.77	1.12	1.75
	1.00	Insoluble	0.43	0.79	1.14	1.76

In all cases the HAD2EH-alkane mixture was heated to 100°C at high pressure while being mixed, followed by cooling to the temperature listed in **Table 2**. The relative viscosity of HAD2EH-thickened solutions of propane and butane is shown in **Fig. 10**. Increasing pressure to values up to 62.05 MPa has little effect on relative viscosity [41], therefore only the relative viscosity results at 6.89 MPa are presented. Surprisingly, only modest decreases in viscosity were observed with increasing target temperature. Further, HAD2EH is a much more effective thickener of butane than propane. For example, at a concentration of 1 wt% HAD2EH in butane at 40°C, the transparent solution is so viscous that the Pyrex ball does not fall, while the viscosity of propane increases only by a factor of 14. At 0.5 wt% HAD2EH and at 100°C, butane is thickened by a factor of 14, while propane viscosity increases by a factor of 3.

Fig. 10. Increase in propane (represented by smooth solid curves) and butane viscosity (represented by smooth dashed curves) caused by HADEH at $P = 6.89$ MPa and average shear rate (Equation 2) of $350 - 7100 \text{ s}^{-1}$. Δ HADEH at 40°C; $\square$ HADEH at 60°C; $\circ$ HADEH at 80°C; $\times$ HADEH at 100°C. (In butane, at concentration of 1.00wt% for $40^\circ\text{C} < T < 100^\circ\text{C}$, the solution was so viscous that the ball did not fall)

3.2.3 Crosslinked Phosphate ester (CPE): Phosphate ester (HGA 70-C6) and cross linker (HGA 65)

This phosphate ester (HGA 70-C6) is soluble to at least 1wt% in high pressure liquid ethane, propane and butane at 25°C at pressures less than 1 MPa above the alkane vapor pressure. However, the HGA 65 cross linker solution is not completely soluble in pentane or in the high pressure ethane, propane or butane. A small amount of a second liquid phase (possibly the solvent used in the preparation of the HGA 65) appears when HGA 65 is combined with any of these alkanes at pressures to 69 MPa. Therefore (unlike the TBTF and HAD2EH solutions), a transparent single phase does *not* result when the phosphate ester and crosslinker are combined in any of the NGL constituents. Rather, at very high pressures these mixtures appear as a slightly hazy, translucent fluids that contain a very small amount of suspended, sub-millimeter droplets. As this mixture is expanded, a pressure is reached where significant precipitation occurs that renders the mixture completely opaque. The pressure at which this occurs is designated as the “cloud point” of the translucent phase.

Table 3 - Cloud point* data for CPE in light alkanes; phosphate ester HGA-70 C6 and cross linker HGA65

Solvent	Combined concentrations (wt%)	Cloud point*		
		(MPa)		
		25°C	40°C	60°C
Ethane	0.25	10.41	10.51	10.69
	0.50	11.10	11.38	11.78
	1.00	15.89	17.00	18.03
Propane	0.25	1.07	1.52	2.29
	0.50	1.07	1.52	2.26

	1.00	1.06	1.48	2.24
n-Butane	0.5	0.28	0.42	0.74
	1.0	0.29	0.42	0.76

*Unlike the TBTF and HAD2EH systems that formed transparent single phases, these CPE cloud point values correspond to the transition from a translucent phase with small suspended droplets to a completely opaque mixture. The relative viscosity of CPE-thickened ethane, propane and butane at pressures above the cloud point pressure of the mixture was determined at 25, 40 and 60°C. In all cases, the small droplets suspended in the thickened alkane have no difficulty flowing around the falling ball, therefore falling ball viscometry was used to estimate viscosity. The ability of the (phosphate ester + crosslinker) mixture to thicken the light alkanes increased slightly with increasing pressure and decreased with increasing temperature [41], therefore the results for ethane, propane and butane are presented in **Figs. 11, 12 and 13**, respectively, only for the pressure of 20.68 MPa.

A very modest viscosity enhancement occurs with the addition of the (phosphate ester + crosslinker) mixture to ethane. For example, at a combined concentration of 1 wt% at 25°C and 20.68 MPa, the viscosity increased by a factor of only 1.9. Greater increases were observed in propane, and the largest viscosity increases occur when butane is thickened. For example, at a combined concentration of 1wt% at 25°C and 20.68 MPa, the viscosity of propane and butane increased by a factor of 3.0 and 5.3, respectively. These increases are much less significant than those attained with CPE in pentane. Further, the CPE-induced viscosity enhancement of the NGL components is much less significant than those realized with either TBTF or HAD2EH.

Fig. 11. Increase in ethane viscosity caused by HGA 70-C6 + HGA 65 at $P = 20.68$ MPa and average shear rate (Equation 2) of $4000 - 7100 \text{ s}^{-1}$. Δ HGA-70 C6 + HGA 65 at 25°C ; $\square$ HGA-70 C6 + HGA 65 at 40°C ; $\circ$ HGA-70 C6 + HGA 65 at 60°C .

Fig. 12. Increase in propane viscosity caused by HGA 70-C6 + HGA 65 at $P = 20.68$ MPa and average shear rate (Equation 2) of $2400 - 7100 \text{ s}^{-1}$. Δ HGA-70 C6 + HGA 65 at 25°C ; $\square$ HGA-70 C6 + HGA 65 at 40°C ; $\circ$ HGA-70 C6 + HGA 65 at 60°C .

Fig. 13. Increase in butane viscosity caused by HGA 70-C6 + HGA 65 at $P = 20.68$ MPa and average shear rate (Equation 2) of $1300 - 7100 \text{ s}^{-1}$. Δ HGA-70 C6 + HGA 65 at 25°C ; $\square$ HGA-70 C6 + HGA 65 at 40°C ; $\circ$ HGA-70 C6 + HGA 65 at 60°C .

4. Conclusions

Three classes of small molecule thickeners were assessed for their ability to dissolve in high pressure ethane, propane and butane and then to induce viscosity changes at temperatures of 25 to 100°C . All viscosity measurements were conducted with a close-clearance falling ball viscometer at pressures above the mixture cloud point. In general, increasing pressure resulted in only slight increases in viscosity, while increasing temperature led to decreases in viscosity due to disruption of intermolecular associations.

Tributyltin fluoride (TBTF) is remarkably effective as a viscosity enhancing agent in that it does not require a heating/cooling cycle to attain dissolution. TBTF dissolves readily in these fluids with several minutes of mixing and, at a concentration of 1wt%, induces nearly 100-fold viscosity increases at a concentration of 1wt% at 25°C . Although much higher pressures were required to dissolve the TBTF in ethane (than in the other fluids), TBTF induces viscosity

changes in ethane that are comparable to those observed for propane and butane. To the best of our knowledge, this is the first time that a small molecule thickener has ever been reported for ethane.

Hydroxyaluminum di-2-ethylhexanoate (HAD2EH) is insoluble in ethane to pressures of 69 MPa and temperatures to 100°C. HAD2EH does not dissolve in propane or butane unless the high pressure mixture of the alkane and HAD2EH are first mixed at about 100°C and then cooled to the temperature of interest. The solution of HAD2EH in propane or butane remains transparent when the system is cooled to temperature as low as 40°C; but at 25°C the HAD2EH precipitates. Relative to TBTF, HAD2EH induces a larger viscosity change at comparable composition and temperature. For example, HAD2EH increases the viscosity of liquid propane by a factor of ~10 at a concentration of 1.0wt% at 100°C, while TBTF at 1wt% and a lower temperature of 60°C increases the viscosity of propane by a factor of only ~6.

A phosphate ester and polyvalent crosslinker combination, LZOS HGA 70-C6 and HGA 65, respectively, exhibits highly desirable attributes for practical application (e.g. low viscosity pump-able liquid components, very fast crosslinking kinetics) and yields substantial viscosity increases for pentane via the formation of an associative phosphate ester network (CPE). However, this two-component mixture did not form a stable, transparent solution in ethane, propane or butane. Rather, a white, translucent fluid formed that contained very fine droplets of a second liquid phase. The “cloud point” for this system is reported as the pressure at which the solution becomes completely opaque upon expansion. Because the ball is able to fall at a terminal velocity through this fluid mixture above the cloud point in a close-clearance falling ball viscometer, relative viscosity can be measured even though the system is not a transparent single phase. At a combined concentration of 1wt% (HGA 70-C6 phosphate ester + HGA 65

crosslinker), 25°C and 20.68 MPa, the viscosity of ethane, propane and butane increase by factors of only 1.9, 3.0 and 5.3 at pressures above the cloud point.

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References

- [1] L. Koottungal, Survey: Miscible CO₂ continues to eclipse steam in US EOR production, Oil & Gas J. 112 (2014) 78.
- [2] J. J. Taber, Technical screening guides for the enhanced recovery of oil, in: Society of Petroleum Engineers annual Technical Conference and Exhibition, One Petro, California, 1983, SPE-12069-MS.
- [3] D. G. Friend, H. Ingham, J. F. Fly, Thermophysical properties of ethane, J. Physical and Chemical Reference Data 20 (1991) 275–347.
- [4] H. Miyamoto, K. Watanabe, A thermodynamic property model for fluid-phase propane, International J. Thermophysics 21 (2000) 1045–1072.

- 455 [5] H. Miyamoto, K. Watanabe, Thermodynamic property model for fluid-phase n-butane,
456 International J. Thermophysics 22 (2001) 459–475.
- 457 [6] D. K. Dandge, C. Taylor, J. P. Heller, K. V. Wilson, N. Brumley, Associative organotin
458 polymers. 2. Solution properties of symmetric trialkyltin fluorides, J. Macromolecular
459 Science 26 (1989) 1451–1464.
- 460 [7] R. M. Enick, The effect of hydroxy aluminum disoaps on the viscosity of light alkanes
461 and carbon dioxide, in: Society of Petroleum Engineers International Symposium on
462 Oilfield Chemistry, California, 1991, SPE 21016-MS.
- 463 [8] K. W. Smith, L. J. Persinski, US Patent 5614010 A, 1997.
- 464 [9] R. S. Taylor, G. P. Funkhouser, US Patent 7314850 B2, 2008.
- 465 [10] P. Dunn, D. Oldfield, Tri-normal-butylin fluoride - a novel coordination polymer in
466 solution, J. Macromolecular Science 4 (1970) 1157–1168.
- 467 [11] A. Iezzi, R. Enick, and J. Brandy, The direct viscosity enhancement of carbon dioxide, in:
468 American Chemical Society symposium series 406 (1989) 122-139.
- 469 [12] J. P. Heller, D. K. Dandge, R. J. Card, L. G. Donaruma, Direct thickeners for mobility
470 control of CO₂ floods, Society of Petroleum Engineers J. 25 (1985) 679–686.
- 471 [13] E. V. Van Den Berghe, G. P. Van Der Kelen, A study of the chemical bond in
472 (CH₃)_nSn(SCH₃)_{4-n} (n=0, 1, 2, 3) by NMR (¹H, ¹¹⁹Sn, ¹³C) spectroscopy, J.
473 Organometallic Chemistry 26 (1971) 207–213.
- 474 [14] L. Fieser, G. Harris, E. Hershberg, M. Morgana, F. Novello, S. Putnam, Napalm,
475 Industrial & Engineering Chemistry Research 38 (1946) 768–773.

- 476 [15] M. Hughes, Napalm: an american biography, War in History 21 (2014) 560–562.
- 477 [16] K. Mysels, Napalm - mixture of aluminum disoaps, Industrial & Engineering Chemistry
478 Research 41 (1949) 1435–1438.
- 479 [17] N. Pilpel, Properties of organic solutions of heavy metal soaps, Chemical Reviews 63
480 (1963) 221–234.
- 481 [18] K. W. Smith, L. J. Persinski, US Patent 5417287 A, 1995.
- 482 [19] K. W. Smith, L. J. Persinski, US Patent 5571315 A, 1996.
- 483 [20] R. S. Taylor, G. P. Funkhouser, US Patent 6511944 B2, 2003.
- 484 [21] R. S. Taylor, G. P. Funkhouser, R. G. Dusterhoft, R. S. Lestz, A. Byrd, US Patent
485 7,341,103 B2, 2008.
- 486 [22] E. Delgado, B. Keown, US Patent 8377854 B2, 2013.
- 487 [23] R. Taylor, A. Khallad, A. Cheng, B. Barree, J. Byrnes, K. Kelly, M. Conway, R.
488 Caufield, S. Tourigny, Optimized gas-well stimulating using CO₂-miscible, viscosified
489 hydrocarbon fracturing fluids, in: Society of Petroleum Engineers Gas Technology
490 Symposium, Alberta, 2002, SPE-75666-MS.
- 491 [24] R. S. Taylor, G. P. Funkhouser, R. G. Dusterhoft, R. S. Lestz, WO Patent, 2,005,083,032
492 A1, 2005.
- 493 [25] G. P. Funkhouser, N. Tonmukayakul, F. Liang, Rheological comparison of
494 organogelators based on iron and aluminum complexes of dodecylmethylphosphinic acid
495 and methyl dodecanephosphonic acid, Langmuir 25 (2009) 8672–8677.

- 496 [26] M. George, G. P. Funkhouser, P. Terech, R. G. Weiss, Organogels with Fe(III)
497 complexes of phosphorus-containing amphiphiles as two-component isothermal gelators,
498 Langmuir 22 (2006) 7885–7893.
- 499 [27] M. George, G. P. Funkhouser, R. G. Weiss, Organogels with complexes of ions and
500 phosphorus-containing amphiphiles as gelators. Spontaneous gelation by in situ
501 complexation, Langmuir 24 (2008) 3537–3544.
- 502 [28] M. G. Page, G. G. Warr, Influence of the structure and composition of mono- and dialkyl
503 phosphate mixtures on aluminum complex organogels, Langmuir 25 (2009) 8810–8816.
- 504 [29] R. E. Hurst, Use of liquified gases as fracture fluids for dry gas reservoirs, in: Society of
505 Petroleum Engineers of AIME, Texas, 1972, SPE-4116-MS.
- 506 [30] C. F. Smith, Gas well fracturing using gelled non-aqueous fluids, in: Society of
507 Petroleum Engineers of AIME, Nevada, 1973, SPE-4678-MS.
- 508 [31] R. S. Taylor, R. S. Lestz, L. Wilson, G. P. Funkhouser, H. Watkins, D. Attaway, Liquid
509 petroleum gas fracturing fluids for unconventional gas reservoirs, in: Canadian
510 International Petroleum Conference, Alberta, 2006, paper 2006-169.
- 511 [32] E. H. Tudor, G. W. Nevison, S. Allen, B. Pike, 100% gelled LPG fracturing process: an
512 alternative to conventional water-based fracturing techniques, in: Society of Petroleum
513 Engineers regional meeting, West Virginia, 2009, SPE-124495-MS.
- 514 [33] R. S. Lestz, L. Wilson, R. S. Taylor, G. P. Funkhouser, H. Watkins, D. Attaway, Liquid
515 petroleum gas fracturing fluids for unconventional gas reservoirs, J. Canadian Petroleum
516 Technology 46 (2007) 68-72.

- 517 [34] R. S. Taylor, R. S. Lestz, D. B. Bennion, G. P. Funkhouser, I. R. Geddes, Rheological
518 evaluations of co miscible hydrocarbon fracturing fluids, J. Canadian Petroleum
519 Technology 44 (2005) 65-69.
- 520 [35] A. Dhuwe, J. Sullivan, J. Lee, A. Klara, S. Cummings, R. Enick, E. Beckman, and R.
521 Perry, Close-clearance high pressure falling ball viscometer assessment of ultra-high
522 molecular weight polymeric thickeners for ethane, propane and butane, J. Petroleum
523 Science and Engineering (2016) submitted.
- 524 [36] L. Hong, E. Fidler, R. Enick, R. Marentis, Tri-tert-butylphenol: a highly CO₂-soluble
525 sand binder, J. Supercritical Fluids 44 (2008) 1–7.
- 526 [37] S. Kilic, S. Michalik, Y. Wang, J. K. Johnson, R. M. Enick, E. J. Beckman, Effect of
527 grafted lewis base groups on the phase behavior of model poly(dimethyl siloxanes) in
528 CO₂, Industrial & Engineering Chemistry Research 42 (2003) 6415–6424.
- 529 [38] M. B. Miller, D.-L. Chen, H.-B. Xie, D. R. Luebke, J. Karl Johnson, R. M. Enick,
530 Solubility of CO₂ in CO₂-philic oligomers; Cosmothem predictions and experimental
531 results, Fluid Phase Equilibria 287 (2009) 26–32.
- 532 [39] Z. H. Huang, C. M. Shi, J. H. Xu, S. Kilic, R. M. Enick, E. J. Beckman, Enhancement of
533 the viscosity of carbon dioxide using styrene/fluoroacrylate copolymers, Macromolecules
534 33 (2000) 5437–5442.
- 535 [40] J. Xu, A. Wlaschin, R. M. Enick, “Thickening carbon dioxide with the fluoroacrylate-
536 styrene copolymer, Society of Petroleum Engineers J. 8 (2003) 85–91.

- 537 [41] A. Dhuwe, Thickeners for natural gas liquids to improve the performance in enhanced oil
538 recovery and fracturing, M.S. thesis, University of Pittsburgh, 2016.
- 539 [42] C. M. Hansen, Hansen solubility parameters: a user's handbook, 2nd ed., CRC, Florida,
540 2007, pp. 347-485.