



## 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 1 wt% 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.

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### 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 CO<sub>2</sub> EOR because most of the CO<sub>2</sub> employed is conveniently obtained from massive natural deposits and is transported through an existing CO<sub>2</sub> distribution pipeline network, whereas the NGLs used for EOR originate in gas processing plants associated with oil recovery projects (including CO<sub>2</sub> 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 CO<sub>2</sub> or methane for EOR, especially because larger supplies of CO<sub>2</sub> or methane may be readily available and significantly less expensive than the NGL themselves. CO<sub>2</sub> 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 CO<sub>2</sub>; 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/cm<sup>3</sup>, 0.5 g/cm<sup>3</sup> and 0.6 g/cm<sup>3</sup> 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

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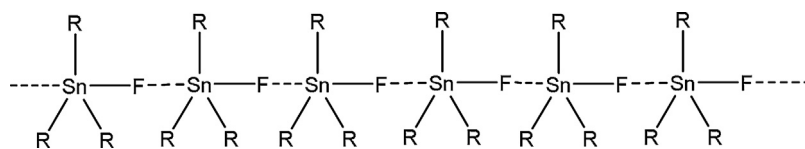


Fig. 1. Association in trialkyltin fluoride.

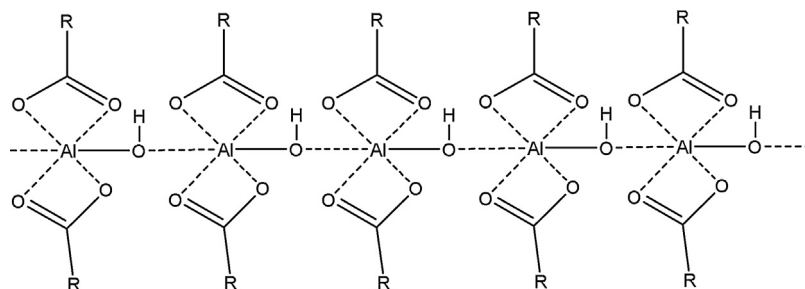


Fig. 2. Possible association of HAD2EH molecules [15].

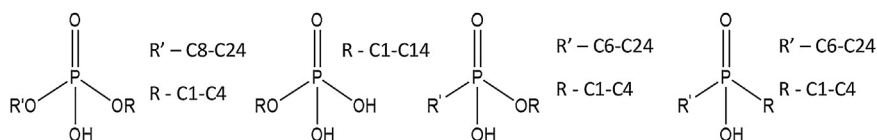


Fig. 3. Phosphate di-ester, Phosphate mono-ester, Phosphonic acid ester and Dialkyl phosphinic acid.

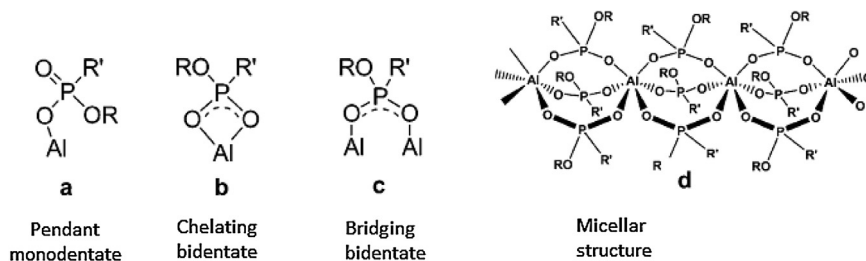


Fig. 4. Mechanism of chelating complex (phosphate ester with metal ion cross linker) [25–28].

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

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