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Direct Gas Thickener

Nasser Mohammed Al Hinai, Matthews Myers, Colin D. Wood and Ali Saeedi

Abstract

Direct gas thickening technique has been developed to control the gas mobility in the miscible gas injection process for enhanced oil recovery. This technique involves increasing the viscosity of the injected gas by adding chemicals that exhibit good solubility in common gasses, such as CO_2 or hydrocarbon (HC) solvents. This chapter presents a review of the latest attempts to thicken CO_2 and/or hydrocarbon gases using various chemical additives, which can be broadly categorised into polymeric, conventional oligomers, and small-molecule self-interacting compounds. In an ideal situation, chemical compounds must be soluble in the dense CO_2 or hydrocarbon solvents and insoluble in both crude oil and brine at reservoir conditions. However, it has been recognised that the use of additives with extraordinary molecular weights for the above purpose would be quite challenging since most of the supercritical fluids are very stable with reduced properties as solvents due to the very low dielectric constant, lack of dipole momentum, and low density. Therefore, one way to attain adequate solubility is to elevate the system pressure and temperature because such conditions give rise to the intermolecular forces between segments or introduce functional groups that undergo self-interacting or intermolecular interactions in the oligomer molecular chains to form a viscosity-enhancing supramolecular network structure in the solution. According to this review, some of the polymers tested to date, such as polydimethylsiloxane, polyfluoroacrylate styrene, and poly(1,1-dihydroperfluorooctyl acrylate), may induce a significant increase of the solvent viscosity at high concentrations. However, the cost and environmental constraints of these materials have made the field application of these thickeners unfeasible. Until now, thickeners composed of small molecules have shown little success to thicken CO_2, because CO_2 is a weak solvent due to its ionic and polar characteristics. However, these thickeners have resulted in promising outcomes when used in light alkane solvents.

Keywords: CO_2, associated gas, NGL, polymer, small molecules, miscible gas injection, thickener, and viscosity

1. Introduction

Over the past 50 years, several research groups have attempted to increase the viscosity of gas-solvents for two purposes. The first purpose is to reduce the gas mobility and improve conformance control for miscible gas injection (MGI). By simply increasing the injected gas viscosity, gas mobility will be reduced, and as a result the sweep efficiency and oil recovery would be improved. The second purpose is to thicken supercritical fracturing fluids to enhance well productivity in tight reservoirs [1–3]. This former application is particularly useful for reservoirs

that are sensitive to the typical water-based fluids used for fracturing. Increasing the fluid viscosity results in a more effective fracturing fluid [1]. In addition, at high pressures, viscous fluids would be able to propagate wider fractures by improving the transport of proppant particles and reducing the leak-off of gas into the faces of the fracture [1, 3, 4].

In previous studies, efforts were centred on identifying thickeners for CO_2 and natural gas liquid (NGL) (i.e. ethane, propane, and butane) thickeners. These attempts are based on polymeric and small-molecule candidates as will be reviewed and highlighted in this chapter. The mechanisms behind the thickening of any solvent depend on polymer coil expansion, intermolecular interactions, entanglement, aggregation (affected by the polymer molecular weight distributions), and self-assembly and indirectly through the effect of polymer molecules on nearby solvent molecules [5].

2. Direct carbon dioxide thickeners

2.1 Polymeric thickeners

The use of a polymer thickener is one of the fundamental strategies for increasing CO_2 viscosity [2]. The main advantages of this approach are that the thickening process can enhance CO_2 viscosity over a wide range of temperatures and improve sweep efficiency across the reservoir formation [6]. Although high molecular weight (Mw) polymers (Mw $>10^6$ g.mol^{-1}) are effective viscosity enhancers at dilute concentrations, it is extremely challenging to dissolve ultrahigh molecular weight in dense CO_2 at reservoir conditions [6, 7]. In the literature, several polymers (Mw: 10^3–10^6 g.mol^{-1}) have been designed and identified that can be dissolved and thicken supercritical CO_2 [1]. However, the pressure required for the dissolution of these polymers is very high in the range of 68.95–275.79 MPa, which is significantly higher than the typical reservoir pressures for CO_2 flooding (MMP, 10.3–27.6 MPa) [1].

The earliest attempts at viscosity enhancers for dense CO_2 were with oil-soluble polymers (e.g. non-polar organic polymers) because CO_2 is known to be a non-polar solvent capable of dissolving certain hydrocarbons and other small molecules quite well [6, 8]. Therefore, it was expected that oil-soluble polymers would be a more likely candidate to dissolve in supercritical CO_2 compared to water-soluble polymers. Heller et al. identified 18 hydrocarbon-type polymers that exhibited encouraging solubility (0.22–10 g/litre) in CO_2 at pressures of 11.7–21.4 MPa and temperatures of 293–331 K [9–14]. Although several polymers showed a slight increase in CO_2 viscosity, none of the studied polymers were capable of enhancing the viscosity of CO_2 significantly to a useful level. This is attributed to low solubility in CO_2 leading to a random polymer coil structure that is not efficient at significantly increasing viscosity. Furthermore, the molecular weight of the polymers found to be soluble in CO_2 was very low. For example, a 1 wt% solution of low molecular weight atactic poly(methyl oxirane) (Mw: 408 g.mol^{-1}) exhibited slight solubility in CO_2 and increased its viscosity by approximately 25% at 301–306 K and 13.7–17.9 MPa [11]. These initial efforts were followed by subsequent attempts to maximise the entropy of mixing between the CO_2 and polymers by using disordered polymers with irregularity in multiple components and side chains that varied in chain length [9]. Thereby, focus was put on poly(α-olefins), such as poly(1-hexene), poly(1-pentene), and poly(1-decene) (P-1-D). Although some achievements were made with some of the evaluated polymers, none of these amorphous polymers were considered to be effective thickeners primarily due to their low solubility in CO_2. In general, it is concluded that the molecular weight of the polymers had to

be fairly low (Mw > 1000 g.mol^{-1}) and thus less effective at enhancing viscosity to achieve significant solubility in CO_2 [6]. Typically, high and ultrahigh molecular weight polymers are used as effective thickeners. In 2012, Zhang et al. reported that less than 1 wt% solutions of two oligomers (i.e. P-1-D and poly(vinyl ethyl ether) (PVEE)) (**Figure 1**) could increase the viscosity of CO_2 by 13–14-fold at 329 K [15]. Previous research groups found that neither a 1 wt% mixture of PVEE nor P-1-D was capable of enhancing the viscosity in either toluene or CO_2 by more than several percents [2, 6, 8]. Therefore, Zhang et al. findings do not correlate and are inconsistent with the results of other research groups. Most previous studies, reported that for low/high molecular weight polymers, a concentration of 1.5–7 wt% is required to thicken CO_2 albeit at very high pressure [6]. In recent studies, [16, 17] P-1-D has been found to have sufficient solubility in both CO_2 and associated gas (AG) mixtures (at temperatures above 358 K and pressures of 50–55 MPa) to considerably increase gas viscosity. The viscosity enhancement of P-1-D in an AG mixture (25 mol% CO_2) and CO_2 was measured in a capillary viscometer at different pressures (50–55 MPa), 377 K, and varying P-1-D concentrations (1.5–9 wt%). For example, at 5 wt% P-1-D, the CO_2 viscosity falls in the range of 0.14–0.18 cP (1.2–2.6-fold) over the pressure range of 50–55 MPa, while over the same pressure range, the AG mixture viscosity is in the range of 0.126–0.131 cP (~4-fold).

In 1987, a patent published by Bullen and co-workers [18] claimed that CO_2-based fracturing could be improved by adding a small amount of a polycarbonate copolymer (Mw: 20,000–150,000 g.mol^{-1}) that was formed via low-temperature reaction of CO_2 with propylene oxide in a homogeneous catalyst (e.g. diethylzinc and/or acetic acid anhydride). This copolymer exhibits dissolution in CO_2 and is capable of increasing its viscosity by threefold at a concentration of 2.5 wt% at 295 K and pressures ranging from 10 to 25 MPa. Furthermore, Sarbu et al. [19] tested the solubility of poly(ether-carbonate) copolymers (derived from propylene oxide and CO_2) in CO_2. They found that this copolymer (Mw: 16000 g/mol) could only be dissolved at 1 wt% at 295 K and 14 MPa. However, there was no significant increase in CO_2 viscosity under these conditions. This calls into question some of the results by Bullen and co-workers as they are much better than later literature [2].

Other researchers have attempted to use entrainers (co-solvents) to improve the solubility of polymers in CO_2 [20] and as such increase the CO_2 viscosity as well as increase the solubility of crude oil components in the CO_2-rich phase [21]. These
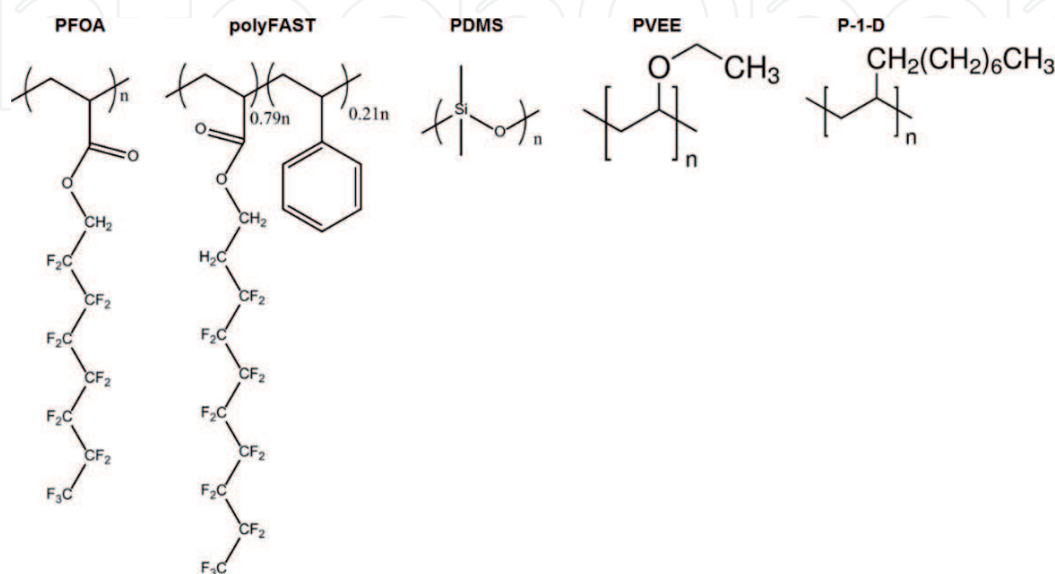

Figure 1.
High/low molecular weight polymeric thickener tested in CO_2 with/without co-solvent [8].

entrainers are relatively low molecular weight non-polar or polar organic compounds which include alcohols, glycols, ethoxylated alcohols, and hydrocarbons [21]. Chullick's patent claimed that addition of alcohol and glycol would promote the solubility of polymers in CO_2 [20]. The rationale is that polar entrainers improve the polarizability of CO_2, which may act in a similar manner to a surfactant in the water/oil system, while non-polar entrainers may function as mutual solvents in a polymer/CO_2 system [20]. Therefore, the addition of entrainers to a supercritical fluid (SCF) leads to increase in the solvent power of SCF [21]. Furthermore, a National Institute for Petroleum and Energy Research (NIPER) group evaluated the use of entrainers (without polymer) as CO_2 thickeners [21]. They reported substantial increase of CO_2 viscosity with high concentration of entrainers in CO_2. For example, 13 mol% of isooctane and 44 mol% of 2-ethylhexanol increased the viscosity of CO_2 by 243 and 1565%, respectively. However, at dilute concentration of entrainers in CO_2, the viscosity enhancement was subtle. For example, 2 mole% of 2-ethylhexanol resulted in 24% of CO_2 viscosity enhancement [21]. In another patent, a treating fluid was used to increase the viscosity of CO_2 solution. This treating fluid is formed by solubilising a polymer or copolymer of dimethylacrylamide (0.25–2.5 wt%) in the substantially anhydrous liquid which was cross-linked by a metal ion source (0.01–2 wt% of titanium, zirconium, and/or aluminium). The substantially anhydrous fluid/polymer and CO_2 solutions formed a single phase and viscosified the fluid (13–30 cP) at temperatures of 338–377 K and pressures of 6.89–12 MPa [22]. Although, there is significant increase in CO_2 viscosities, the amount of entrainers added is extremely high [6].

A group of researchers at the University of Wyoming attempted at in situ polymerisation of CO_2-soluble alkene monomers, including ethylene, octene, and decene [23]. They found that polymerised monomers could be miscible in CO_2 at the tested conditions (306 K and 17.9 MPa). However, the polymers did not form stable solutions and produced solid precipitates over time. As a result, viscosity enhancement was not observed. In an attempt to obtain a very high molecular weight polymeric thickener for CO_2, researchers at Chevron [24–26] have assessed candidates that exhibited Hildebrand solubility parameters of less than 7 (cal/cc)$^{0.5}$ that is closer to the CO_2 solubility parameter at reservoir conditions (327 K and 17.2 MPa), which is approximately 6 (cal/cc)$^{0.5}$ [27]. Furthermore, they found beneficial, if the polymer candidates contained electron donor atoms such as oxygen, nitrogen, and sulphur that are capable of interacting favourably with the carbon atom (i.e. an electron acceptor) within the CO_2 molecules. Electron donor functional groups used in this study included ethers, sulphones, siloxanes, thioethers, silyethers, esters, carbonyls, dialkylamides, and tertiary amines. The researchers concluded that such functional groups associated within polymers would enhance the solubility of the polymers to some extent through specific interaction with CO_2. However, full dissolution of such polymers in CO_2 could not be attained without the addition of toluene as a co-solvent [24].

High molecular weight polydimethylsiloxane (PDMS, Mw: 135,000 g.mol^{-1}) (**Figure 1**) was initially tested by Heller et al. [11] for solubility in CO_2. They found that 0.03 wt% of PDMS could dissolve in CO_2 at 298 K and 18.9 MPa. However, at this dilute concentration, PDMS did not appreciably enhance CO_2 viscosity. Furthermore, others attempted to increase the PDMS concentrations in CO_2; however, the solubility of PDMS in CO_2 could not be attained without substantial addition of toluene as a co-solvent. Therefore, it was determined that very high molecular weight PDMS (Mw: 197,000 g.mol^{-1} and 7.3 (cal/cc)$^{0.5}$) could effectively thicken CO_2 only if a toluene co-solvent (10–20%) was added into the solution [26]. For example, addition of 20 wt% toluene co-solvent enabled up to 4 wt% of PDMS to be dissolved in CO_2, resulting in a 30-fold of CO_2 viscosity enhancement [26].

This viscosity enhancement was compared only with pure CO_2 viscosity, but it was not compared against toluene/CO_2 viscosity, because it was expected that toluene addition into CO_2 may not contribute directly to the CO_2 viscosity enhancement and it only improves the solubility of polymer in CO_2. However, their core flooding experiment results showed that CO_2/toluene flood gives higher oil recovery than pure CO_2 flood. This attributes to that toluene is a strong solvent, which causes a higher oil swelling and oil viscosity reduction. It was also found the viscous solution (20 wt% toluene, 4 wt% of PDMS, and 76 wt% of CO_2) can significantly reduce gas mobility, increase oil recovery (10–20%), and delay the breakthrough in porous media. In another study a group of researchers from Texas A&M University added an organic co-solvent (e.g. toluene) into CO_2-philic polymeric thickeners (PDMS and polyvinyl acetate (PVAc)) during core flooding experiments in order to enhance the solubility in CO_2 [28, 29]. They prepared solutions of PDMS (5 wt% with a Mw of 260,000 g.mol^{-1}) and PVAc (5 wt% with a Mw of 170,000 g.mol^{-1}) with a range of toluene concentrations from 10 to 20 wt% added as a co-solvent. In addition, PVEE was used at the concentration of 0.8 wt% in CO_2 without the addition of a co-solvent, as this polymer has the ability to dissolve in CO_2 without a co-solvent [29]. Their results proved that PDMS and PVAc with the addition of toluene could improve the gas mobility, accelerate the oil recovery (5–10% with PDMS and 4–9% with PVAc), and delay CO_2 breakthrough. These results were consistent with the finding of Chevron researchers that 4 wt% PDMS was soluble and could thicken CO_2 in the presence of a co-solvent. In other words, both groups found that PDMS and PVAc are both to be CO_2-philic and effective thickeners with the use of substantial amounts of a co-solvent. PVEE (Mw: 3800 g.mol^{-1}) at low concentration (0.8 wt%) did not show any increase in viscosity or improvement in CO_2 mobility and oil recovery [29]. This means that the PVEE may not be able to increase the CO_2 viscosity at this concentration which further confirms that the thickening level reported by Zhang et.al is higher than expected.

A group of researchers at the New Mexico Petroleum Recovery Research Center (PRRC) proposed another route towards high-performance thickeners by introducing self-interacting functional groups at each end of the polymer chains [14]. These polymers with terminal ionic groups (linear, difunctional, and telechelic ionomers) were thought to be effective thickeners in non-polar solvents as the ionic groups in each chain could aggregate into multiple ion pairs causing interaction between separate chains. They incorporated sulphonate groups onto the ends of polyisobutylene, and although this polymer is soluble in CO_2 at a concentration of 0.4 wt%, the sulphonated ionomer was only partially dissolved in CO_2, which is a weak solvent for this ionic group. In a recent publication, O'Brien et.al [30] used a route similar to the approach proposed by the PRRC group. The difference between the two studies is that the PRRC group used functional groups in the polymer chain that experiences intermolecular interactions with CO_2, while O'Brien proposes using functional groups that form self-assembly and intermolecular interactions via hydrogen bonding (donor-acceptor), π-π stacking, and dipole-dipole interactions. Therefore, the strategy used by the O'Brien's group could be used to explore oligomeric molecules. So, they synthesised a series of aromatic-amide terminated PDMS oligomers (i.e. low molecular weight polymers) to maximise the entropic characteristics for oligomeric species interacting with CO_2 by choosing a solute with high free volume and flexible chains. In addition, the aromatic moieties promote the formation of supramolecular structures among the low molecular weight oligomers. Amide and aromatic amide further enhance this interaction and induce self-assembly through strong hydrogen bond donor-acceptor interactions. The researchers found that amide-terminated-PDMS oligomers with simple aromatic groups through the incorporation of electron-deficient aromatic groups onto these

amides (i.e. 4-nitrobenzamide, biphenyl-4-carboxamide, and anthraquinone-2-carboxamide) did not show any significant impact on CO_2 viscosity at a concentration of 1 wt% due to the poor interaction of functional groups in these compounds with CO_2. However, they achieved promising results with anthraquinone-2-carboxamide (AQCA) as an end group that was found to be a gelator of hexane at a concentration of 15 wt%, and at concentrations ranging from 5 to 10 wt% in hexane, a significant increase in viscosity was observed. However, this behaviour did not extend to other similar compounds based on either biphenyl-4-carboxamide or 4-nitrobenzamide end groups. Therefore, they attempted to improve the intermolecular interaction with the AQCA end group by utilising branched anthraquinone amides, where the number of AQCA end groups per molecule can be increased. It was found that branched anthraquinone amides were insoluble in CO_2 at concentrations of 1 wt%. However, it was soluble in CO_2 when hexane as co-solvent was added. Hence, this branched compound can be a useful thickener in the presence of substantial amount of hexane as co-solvent. For example, at a temperature and pressure of 348 K and 34.5 MPa, respectively, a transparent solution composed of 13.3% branched anthraquinone-amide functionalised oligomers, 26.7% hexane, and 60% CO_2 was found to have a viscosity three times greater than that of a CO_2/hexane mixture without a thickener. Given the low-viscosity enhancement (threefold) and high concentration of this compound and the co-solvent required, this compound was not considered to be economical and practical for CO_2 flooding. These compounds that have considerable intermolecular interactions with CO_2 are further discussed in the next section of this chapter. Overall, all studies found that high/low molecular weight PDMS polymers were more CO_2-philic than hydrocarbon-based polymers [31], although they were not capable of viscosifying CO_2 without the use of substantial amounts of a co-solvent. However, the high cost of PDMS polymer/ oligomer and high concentration of co-solvent required make the field application for this polymer impractical [2, 6, 7].

DeSimone's research group [32] was arguably among the first to report on a high molecular weight polymer-based CO_2 thickener capable of increasing the viscosity without the need of a co-solvent. They found that 3.4 wt/vol% of either poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) (**Figure 1**) or polyfluoroacylate (PFA, Mw: 1,400,000 g.mol^{-1}) could be dissolved in CO_2 increasing the viscosity of CO_2 by a factor of 2.5 at a pressure of 31 MPa and temperature of 323 K. **Figure 2** shows the increase in CO_2 viscosity resulted from dissolving 3.7 and 6.7 wt/v% of PFOA at 323 K. This is the first example of high Mw polymers that can be dissolved in CO_2 and significantly thicken CO_2 in the absence of a co-solvent. To date, PFOA is still recognised as the most soluble polymer in CO_2 and among the most effective thickeners of CO_2. Unfortunately, PFOA is a fluoropolymer type, which makes it relatively expensive. Furthermore, fluorinated polymers possess environmental concerns as they are suspected as carcinogen [33]. Therefore, if the cost and environmental constraints are considered, PFOA is not practical for field application in CO_2 flooding [2].

To limit these negative aspects of fluorinated polymers and potentially make them viable, Enick and Beckman and other co-workers at the University of Pittsburgh have tried to reduce the amount of fluorinated polymers needed without affecting its performance [4, 34, 35]. They prepared a copolymer based on a perfluoropolyacrylate and a functional group, which engages strongly in intermolecular interactions, in order to promote an increase in CO_2 viscosity. This copolymer is composed of 71–79 mol% of fluoroacrylate monomer (1,1,2,2-ttatra-hydro heptaecfluorodecylacrylate) and 21–29 mol% of styrene group (polyfluoro-acrylate styrene or polyFAST) (**Figure 1**). The fluoroacrylate monomer is highly CO_2-philic and facilitates polyFAST solubility in CO_2. The associating styrene
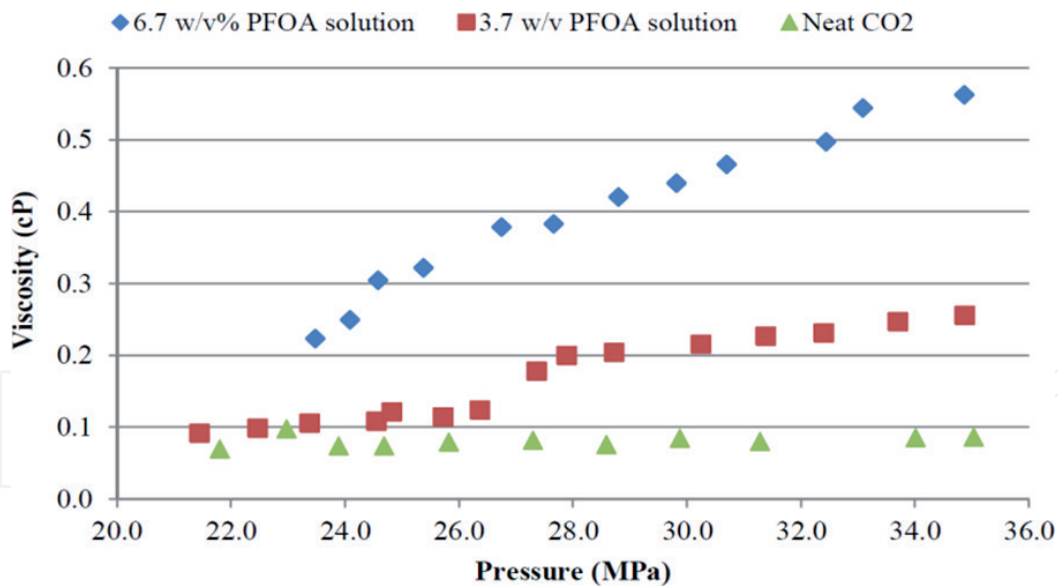
Figure 2.
The viscosity enhancements of PFOA in CO_2 at different pressures and concentrations and temperature of 323 K [32].
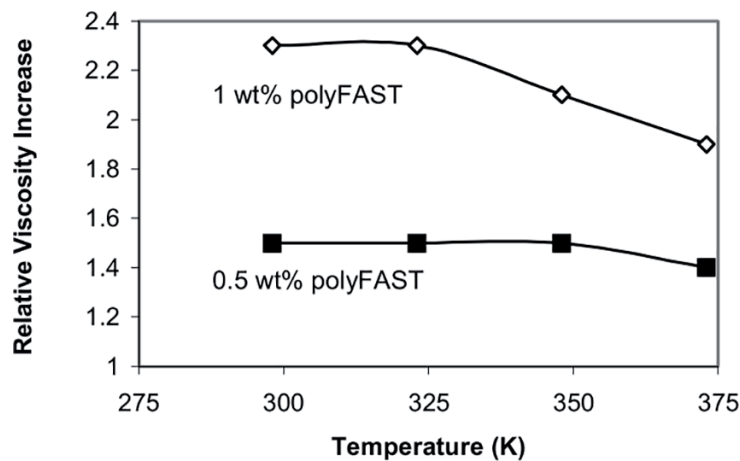

Figure 3.
The effect of temperature on the relative viscosity of polyFAST in CO_2 solution at 34 MPa [35].

group is a mildly CO_2 phobic monomer that promotes intermolecular interactions and improves viscosity enhancement through supramolecular interactions. This copolymer was found to be soluble in CO_2 at pressure and temperature conditions close to those used in CO_2-EOR [34]. However, the solubility was found to decrease with an increase in the styrene content [4]. For instance, the cloud point pressure of 1 wt% of 29 mol% styrene-71 mol% fluoroacrylate copolymer and 35 mol% styrene-71 mol% fluoroacrylate copolymer in CO_2 at 297 K is 12 MPa and 16.2 MPa, respectively. Furthermore, it was also found to significantly increase CO_2 viscosity at dilute concentrations of polyFAST. As it can be seen in **Figure 3**, 0.5 and 1 wt% of polyFAST in CO_2 at 298 K are able to increase the viscosity of CO_2 by 1.5- and 2.3-fold, respectively [34]. However, polyFAST is the most effective polymeric thickener for CO_2 at dilute concentration in the absence of a co-solvent. Comparing to PFOA results, this copolymer was successful to reduce concentration by 73% to achieve the same viscosity improvement (2.3-fold) at 323 K and 34 MPa. However, it was not practical to be used for CO_2-EOR application due to the cost of the copolymer (roughly $132 per kg) and lack of its availability in large quantities [2]. In addition, this copolymer contains a large amount of fluorine, which is environmentally and biologically persistent [29].

Another promising strategy to obtain effective CO_2 thickeners was introduced to avoid the aforementioned environmental and economic concerns associated with fluorous and silicone-based polymers. Several researchers have focused on the synthesis and design of non-fluorinated oligomers and polymers. Tapriyal et al. [36] found that PVAc is the second most CO_2 soluble polymer among non-fluorous polymers with PDMS being the most soluble. However, the dissolution of high Mw PVAc in CO_2 requires a very high pressure. In addition, no measureable viscosity increase was observed with 1–2 wt% of PVAc (Mw: 11000 g.mol^{-1}) in CO_2 at 298 K and 64 MPa. Furthermore, Enick and co-workers [36] designed a non-fluorinated version of PFOA in the hope of finding a thickener candidate that is cheap, environmentally friendly, and capable of increasing CO_2 viscosity at low concentration. Therefore, they developed new copolymers based on an oxygenated hydrocarbon polymer (making it CO_2-philic) and a self-interacting group (or CO_2-phobic) to enhance viscosity. Some of the attractive oxygenated hydrocarbon monomers include vinyl acetate, alkyl vinyl ether, carbonyl, and sugar acetate functional groups [37–43]. Oxygenated hydrocarbon monomers containing functional groups with one or more oxygen atoms can induce thermodynamic interactions with CO_2. These oxygen atoms are electropositive, while the carbon atoms in CO_2 are electronegative, which facilities Lewis acid-base interactions. In addition, the hydrogen bond in the polymer backbone or side chain having increased the positive charge (H¨O) acts as Lewis acids towards electron the oxygen atoms in CO_2 [41]. As mentioned above, PVAc is among the most CO_2-philic high MW oxygenated hydrocarbon polymers [43]. Therefore, Enick and co-workers replaced the fluoroacrylates in polyFAST with vinyl acetate monomers in order to reduce the cost of the polymer. They designed non-fluorous copolymers for CO_2 solubility, while the styrene group was replaced with a benzoyl group for intermolecular association. This approach simplifies the copolymer synthesis as styrene cannot be polymerised with the vinyl acetate monomer due to the large reactivity ratio difference [36]. They synthesised a 5% benzoyl-95% vinyl acetate copolymer or polyBOVA (Mw: 7840 g.mol^{-1}). A modest increase in CO_2 viscosity of 40–80% at a concentration of a 1 and 2 wt% was observed; however, high pressure was required (64 MPa) to attain the dissolution of this copolymer in CO_2 at 298 K.

2.2 Small-molecule self-associating thickeners

An alternate strategy to increase the viscosity of CO_2 is to employ self-interacting low molecular weight compounds as thickeners (**Table 1**). In order to differentiate between co-solvents and this class of thickeners, these compounds interact with each other and the CO_2 resulting in a self-assembled structure that contains a solvent-philic group and a solvent-phobic segment, while a co-solvent is nonassociating and consists of solely a solvent-philic segment [7]. These small molecules do not have the required molecular weight to substantially increase the gas viscosity; however, these compounds self-associate forming a supramolecular network that enhances the CO_2 viscosity [2]. In general, these compounds contain functional groups with both CO_2-philic segments that promote dissolution, and the CO_2-phobic moieties induce intermolecular association [44]. Therefore, the various associations between neighbouring molecules within the CO_2 matrix lead to viscosity enhancement [2]. Furthermore, the self-assembly of these molecules in solution can be characterised via a dramatic viscosity change or small-angle neutron scattering (SANS), FT-IR, circular dichroism, X-ray diffraction, electron microscopy, or differential scanning calorimetry [45–53]. To date, small associative molecules have yielded little success in thickening CO_2, because CO_2 is a poor solvent for these ionic and polar associating groups [8]. The following section describes the different types of small molecules used to thicken CO_2.

Small-molecule compound	Concentration in CO_2	Co-solvent	Soluble in CO_2 observations	CO_2 viscosity increased at 298–313 K	Reference
Trialkyltin fluoride	0.13 wt%	Pentane (39 wt%)	Insoluble	No viscosity increased	[56]
Semi-fluorinated trialkyltin fluorides and fluorinated telechelic ionomers	2–4 wt%	No co-solvent	Soluble	2–3-fold	[55]
Hydroxyaluminum disoaps	—	—	Insoluble	No	[62]
Fluorinated hydroxyaluminum disoaps	—	—	Partially soluble	No	[2]
Metallic stearate powders	—	—	Insoluble	No	[62, 63]
Semi-fluorinated powders	5–20 wt%	No co-solvent	Soluble	Gel solution	[64]
Hydroxystearic acid	3 wt%	Ethanol (15 wt%)	Soluble	100-fold (gel solution)	[65]
Fluorinated bis-ureas	5 wt%	No co-solvent	Soluble	3–5-fold	[66]
Non-fluorous bis-ureas	1 wt%	No co-solvent	Soluble (opaque solution)	No viscosity measured	[67]
Sodium pentadecfluoro-5-dodecyl sulphate (NaF_7H_4)	4.4 wt% NaF_7H_4 10 mol of water/mol surfactant	No co-solvent	Soluble	2-fold	[70]
Nickel bis-nonofluoropentane sulphosuccinate ($Ni-diHCF_4$)	6 wt% $Ni-diHCF_4$ 10 mol of water/mol of surfactant	No co-solvent	Soluble	1.5-fold	[49]
Branched benzene trisurea	0.5–2 wt%	Hexanes (18–48.4 wt%)	Soluble	3–300-fold	[75]

Table 1.
Outline of the solubility in CO_2 and CO_2 thickening capability of small-molecule compound.

2.2.1 Trialkyltin fluorides and semi-fluorinated trialkyltin fluorides

Heller and co-workers studied a series of trialkyltin fluoride compounds as light alkane and CO_2 thickeners [12, 13, 44]. These compounds show a moderate increase in CO_2 viscosity via the formation of intermolecular associations between the tin and fluorine atoms in the solution. **Figure 4** shows the association of tributyltin fluoride molecules. Trialkyltin fluoride forms a long linear transient polymeric chain through intermolecular association between the tin atom and the fluorine
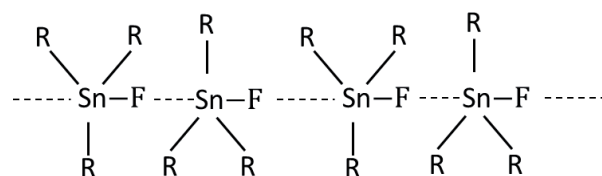
Figure 4.
Association mechanism of tributyltin fluoride [54].

atom of neighbouring molecules. In fact, the tin atom is slightly electropositive which interacts with the electronegative fluorine atom to form an intermolecular Sn-F association, as can be seen in **Figure 4**, while the hydrocarbon arms branching from the tin atom enhance the free volume which facilitates the solubility in CO_2 [55]. Apparently, these molecular structures form linear and associating structures in which the alkyl arms stabilise the aggregation, while the tin atoms in each molecule associate with the fluorine atoms in adjacent neighbour molecules [55]. Although there was some success with tributyltin fluoride or other trialkyltin fluorides in thickening light alkane components, these compounds were insoluble in CO_2 and ineffective as thickeners, even with the addition of pentane as a co-solvent [56, 57]. Later on, Shi et al. [55] synthesised semi-fluorinated trialkyltin fluorides and fluorinated telechelic ionomers to prepare a solution containing both CO_2-philic fluorinated groups to enhance the solubility and CO_2-phobic associating group to promote intramolecular association for viscosity enhancement. Both ionomers were soluble in CO_2 at 2–4 wt% without requiring the addition of a co-solvent. Their results indicated that both ionomers were capable of increasing the viscosity of CO_2 by 2–3-fold over a concentration range of 2–4 wt%. For example, at 4 wt% of tri(2-perfluorobutyl ethyl) tin fluoride in CO_2, the viscosity increased three times at 298 K and 16.5 MPa. This viscosity increase was found to be much less than expected because the side chain fluorine atoms on the Sn-F associations were disrupted. This is attributed to the fluorine atom at the end alky arms competing with the fluorine atom attached to the tin atom caused by the electronegativity differences between these chain-end fluorines and those adjacent to the tin. Hence, the disruption of the fluorinated alkyl chains is responsible for the viscosity increase [55]. Overall, given the necessary high concentrations of the ionomers required and their high costs, these fluorinate oligomers are not considered viable thickeners for field applications [2, 6, 55].

2.2.2 Fluorinated and non-fluorous hydroxyaluminum disoaps

Hydroxyaluminum disoaps were developed to thicken gasoline which was used to make napalm, the infamous weapon type used in World War II [58–60]. These molecules are an aluminium-based soap with two carboxylic acid groups linked to the aluminium atom [61]. A small amount of hydroxyaluminum disoap added to low-viscosity gasoline transforms it to a thick and extremely viscous fluid referred as napalm. In an analogous manner, these compounds were studied to determine their solubility in CO_2 and quantify their ability to thicken CO_2. Enick and co-workers synthesised a series of hydroxyaluminum disoaps [62]. Unfortunately, none of the hydroxyaluminum disoaps were soluble in CO_2. Similar to the results with trialkyl tin compounds summarised above, unpublished results by Enick showed that the solubility of some of these compounds in CO_2 could be enhanced either by fluorinating the alkyl arms or using highly branched alkyl chains [2]. However, this trial has not been successful in fully dissolving the hydroxyaluminum disoaps in CO_2 [2]. Another attempt to thicken CO_2 was done by heating a mixture of CO_2 and

metallic stearate powders [63]. Metal stearates are salts that are produced from the reaction of stearic acid and metal oxide, which are dissolved in hydrocarbon-based oils usually with the assistance of heat to break up strong intermolecular forces. The viscosity of the hydrocarbon-based oils is enhanced when the solution cools down. This same approach was attempted with CO_2; however, this was unsuccessful as they are insoluble even with the assistance of heat.

2.2.3 Semi-fluorinated alkanes

Iezzi and co-workers [64] made an early attempt to thickened CO_2 by using semi-fluorinated alkanes. They designed a series of linear diblock alkane compounds ($F(CF_2)_n (CH_2)_m H$), which contained two immiscible segments forced to interact via a covalent carbon-carbon bond. It is found that this compound can gel organic liquid (e.g. decane and octane) through the formation of micro-fibrillar network if the solution is heated and then left to cool down. After the solution (CO_2 and semi-fluorinated alkane) cools, the semi-fluorinated compounds form a covalent cross-link between molecules and high-porosity and micro-fibrillar networks that can gel the dense CO_2. The fluorinated segments stack with other adjacent fluorinated segments (analogous to hydrocarbon segments) to form the fibre network [7, 56]. However, the gel solution is not suitable for gas mobility control due to its phase behaviour where the viscous solution could not flow through a porous medium and retained at the surface of the rock. This solution may be applicable for conformance control to block fractures or high permeable zones.

2.2.4 Hydroxystearic acid

Heller and co-workers [65] proposed a small organic compound, known as 12-hydroxystearic acid (HAS). This compound ($H_3C(CH_2)_5 CHOH(CH_2)_{10}COOH$) had previously been used to gel hydrocarbon and chlorinated solvents. However, the essential assessment results indicated that the HAS was insoluble in CO_2 unless a significant amount of a co-solvent (i.e. ethanol) was added. For instance, the addition of 15 wt% of ethanol co-solvent enabled a solubility of up to 3 wt% of HAS in CO_2 resulting in a nearly 100-fold increase in viscosity in the temperature range of 300–307 K. As the temperatures decrease, the solution exhibits a slight viscosity increase. In addition, microfibres in the gel solution form an opaque solution that would probably impede the fluid flow in the reservoir formation.

2.2.5 Fluorinated and non-fluorinated bis-ureas

A group of researchers at Yale University and the University of Pittsburgh developed a series of small-molecule compounds containing either one or two urea groups [66]. The urea groups in these compounds induce self-assembly interactions via a hydrogen bond; thereby, these interactions form macromolecular associations that can enhance the viscosity of the CO_2-rich solution. Out of the 12 compounds tested, 4 fluorinated bis-urea compounds were highly soluble in CO_2 without needing heat and capable of improving the CO_2 viscosity by 3–5-fold at 5 wt% of bis-urea at 298 K and 31 MPa. In the hope of obtaining a non-fluorous bis-urea, Paik et al. [67] attempted to incorporate the CO_2-philic groups (hydrocarbon, carbonyl, and ether groups) into the molecular structure of the bis-urea as illustrated in **Figure 5**. However, their results revealed that after forming a transparent solution, microfibres began to form slowly due to the molecules undergoing self-assembly

and precipitating out of solution. Therefore, these compounds cannot be considered for EOR applications.

2.2.6 Surfactants with twin and divalent metal cations

Eastoe and co-workers designed semi-fluorinated surfactants based on a previous study that used aerosol-OT (AOT)-based water-in-oil microemulsions in cyclohexane solvent [49, 68, 69]. The molecular structure of these surfactants is illustrated in **Figure 6**. These surfactants are soluble in CO_2 and form rodlike micelles that enhance CO_2 viscosity with the addition of a small amount of water. The purpose of adding water into the solution is to form a stable microemulsion in the presence of AOT surfactant and to promote an aggregate shape that changes the self-association of the surfactant from a spheroid (non-viscous) configuration to a rod shape (viscous) that significantly enhances the viscosity of the solution. Two di-chain perfluorinated sulphosuccinate surfactants (nickel bis-nonofluoropentane sulphosuccinate (Ni-diHCF$_4$) and sodium pentadecfluoro-5-dodecyl sulphate (NaF$_7$H$_4$)) yielded the greatest viscosity increase among the compounds tested. These surfactants have been modified in such a way that can form rod-like micelles to promote solubility in CO_2 and viscosity enhancement. This was achieved by the exchange of Na^+ ions with Ni^{2+} or Co^{2+} to drive a sphere-to-rod
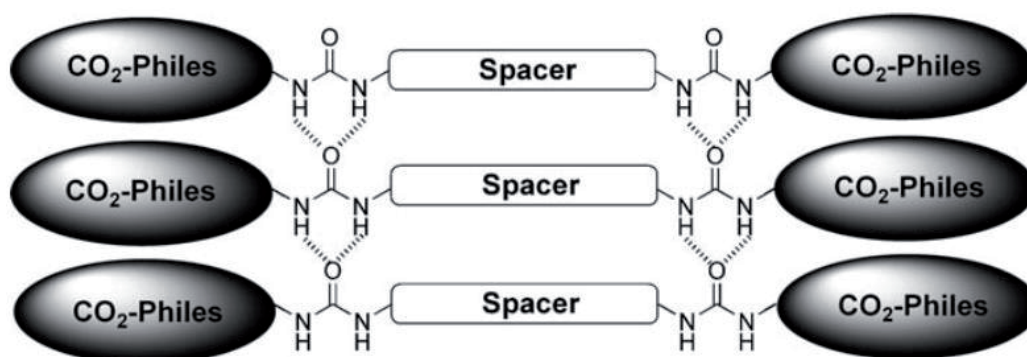

Figure 5.
Molecular structure of non-fluorous bis-ureas [67].
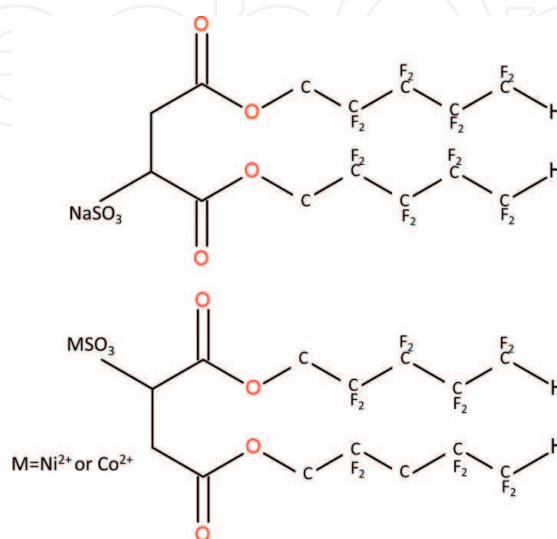

Figure 6.
Molecular structure of a fluorinated twin-tailed surfactant as a CO_2 thickener [49].

transition as shown in **Figure 6** [49, 70]. Furthermore, a di-chain perfluorinated AOT analogue is known to stabilise microemulsions of water in CO_2 [71–74]. A high-pressure small-angle neutron scattering (SANS) confirmed the solubility of both surfactant in CO_2 and formation of rodlike micelles. At 298 K and 40 MPa, both surfactants (0.05 mol dm^{-3}) with 10–12.5 moles of water per mole of surfactant achieved a transparent solution in CO_2 [49, 70]. At 298 K, 35 Mpa, 6 wt% of Ni-diHCF$_4$, and 10 moles of water per mole of surfactant added into CO_2, viscosity enhancements of up to 1.5-fold have resulted [49], and 4.4 wt% of NaF$_7$H$_4$ with 12.5 moles of water per mole of surfactant caused a 2-fold increase in viscosity at 313 K and 40 MPa [70]. However, these surfactants required a very high pressure to attain a single phase, and high concentrations of 5–7 wt% were necessary to achieve a significant viscosity increase. Therefore, these thickeners would not be suitable for field applications as both need a relatively high concentration of these expansive surfactants.

2.2.7 Cyclic and aromatic amide and urea based

Most of the successful associating small-molecule compounds as CO_2 thickeners that have been described above are fluorinated or semi-fluorinated materials. These fluorinated materials are both expensive and environmentally persistent due to the fluorine content and high concentrations (3–5 wt%) required for use as a CO_2-EOR thickener [75]. Therefore, in a recent publication, Doherty et al. [75] synthesised and examined a series of cyclic and aromatic amide and urea compounds as non-fluorous small-molecule thickeners for dense CO_2 and organic liquids. They designed the molecular structure of the compounds as shown in **Figure 7**. These compounds contain cyclic or aromatic core molecules (e.g. cyclohexane or benzene) which are mildly CO_2-phobic to promote intermolecular interactions. These core ring groups are combined with associating or linking groups (labelled as 'X') which are typically either amide, urea, or ester groups to establish the intermolecular interaction for viscosity enhancement. In addition, these linking groups also aid the connection of CO_2-philic segments (siloxane or heavily acetylated) to cyclic or aromatic core molecules to improve dissolution in CO_2. It has been found that after heating and cooling the mixture, these compounds were capable of thickening organic liquids such as hexane and toluene. Researchers have found branched benzene trisurea (propyltris(trimethylsiloxy)silane-functionalised benzene trisurea and trisurea compounds functionalised with varying proportions of propyltris(trimethylsiloxy)silane and propyl poly(dimethylsiloxane)-butyl groups), which are soluble in dense CO_2. These compounds are capable of thickening CO_2 (3–300-fold) at remarkably low concentrations (0.5–2 wt%) in the presence of hexane as a co-solvent at high concentrations (18–48 wt%) [2, 8]. A 300-fold viscosity increase is too large and definitely not suitable for EOR applications. The high concentration of the required co-solvent at low concentration of the additive severely limits the applicability of this approach due to the high manufacturing costs and environmental concerns (**Table 1**).
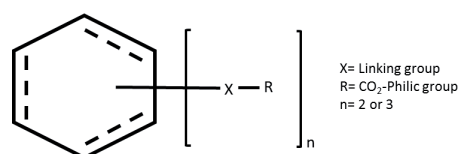

Figure 7.
General molecular structure of small-molecule cyclic amide and urea based [75].

3. Hydrocarbon gas thickeners

3.1 Polymeric thickeners

As discussed so far, most of the research regarding gas thickening agents have focused solely on CO_2 because it is the most common injected fluid for MGI projects in the United States, Canada, and elsewhere [76, 77]. In addition, CO_2 is a slightly more powerful polymer solvent than short-chain alkane gases. The structural symmetry of CO_2 results in a substantial quadruple moment (Q_i) at low pressure and temperature, which can magnify the quadrupole interaction by scale inversely with the molar volume to the 5/6 power ($Q_i^* = Q_i . V_i^{-5/6}$) [78]. Despite these characteristics, CO_2 is a weak solvent when compared to most organic solvents. However, there have been a few attempts at identifying polymeric thickeners for pure light hydrocarbon gases [79–81]. In the late 1960s, several patents reported initial attempts at thickening light alkane gases. Henderson et al. [81] made the first attempt to thicken a hydrocarbon by using three polymers including poly methyl laurylate, polybutadiene, and poly(alkyl styrene). These polymers (at a concentration of 0.25 vol%) are capable of improving the viscosity of light hydrocarbon gases by about 0.1%. Subsequently, Durben and co-workers examined polyisobutylene polymer (PIB, Mw: 130,000 g.mol^{-1}) in a rich condensate mixture containing 75 vol% propane and 25 vol% heptane. They claimed to achieve a 2–5-fold viscosity increase at a concentration of 0.25 wt% of PIB [80]. However, none of the patented work reported the details of the method used to measure the viscosity of the solutions examined.

Subsequent attempts by Heller et al. to identify polymeric thickeners for LPG and CO_2 [9] found that various poly-α-olefin polymers (PAO) based on n-pentene, n-hexene, and n-decene could be used. These polymers were found to be quite soluble in n-butane at a temperature of 298 K and pressure of 8.2 MPa; however, their solubility in CO_2 was much more limited at a temperature of 305 K and pressure of 17.2 MPa. The addition of these polymers at concentrations ranging from 1 to 2.2 wt% to n-butane enhanced the viscosity by fivefold (**Table 2**). In a recent publication, Dhuwe et al. assessed the solubility and viscosity-enhancing property of high and ultrahigh molecular weight polymers in NGL (i.e. a mixture of ethane, propane, and butane) [82, 83]. Polymers evaluated included ultrahigh molecular weight drag-reducing agent (DRA) poly-α-olefin (Mw: 20,000,000 g.mol^{-1}), high molecular weight PDMS (Mw: 980,000 g.mol^{-1}), and PIB (Mw: 130,000 g.mol^{-1}). Ultrahigh molecular weight DRA poly-α-olefin is commonly used in oil pipelines to supress the energy dissipation near the pipe wall that results from the turbulent flow at high flow rates. This polymer does not change the fluid properties (e.g. viscosity) at the dilute concentrations used for this application. Dhuwe et al. [83] found it to be sufficiently soluble in NGL if a significant amount of hexane is added as a co-solvent. For example, at 0.5 wt% of DRA polymer and 24.5 wt% hexane in propane or butane, the cloud point pressures at temperatures of 333 K were found to be equal to 3.07 and 0.77 MPa, respectively. However, it requires very high pressure to attain solubility in ethane (46.95 MPa) at the same concentrations. At 0.5 wt% of DRA polymer and 24.5 wt% of hexane, the viscosity of ethane and propane could be improved by 3–9-fold, while 23–30-fold enhancement was obtained in butane (**Table 2**). The reason for the greater increase in the viscosity of butane is explained by the larger butane solubility compared to the solubility of propane and ethane that aids the expansion of the polymer backbone (i.e. coil) that swells the DRA polymer [82, 83].

Furthermore, they have also tested the solubility of high molecular weight PIB and PDMS in NGL components. PIB was found to be insoluble in ethane, propane, and butane at temperatures ranging from 298 to 353 K and high pressure, while PDMS was soluble in all NGL constituents without the aid of a co-solvent [82, 83].

Small-molecule compound	Concentration in NGL components (wt%)	Co-solvent	Soluble in NGL observations			Relative viscosity at 298–333 K			Ref.
			C_2H_6	C_3H_8	C_4H_{10}	C_2H_6	C_3H_8	C_4H_{10}	
Poly(1-pentene), poly(1-hexene), and poly(1-decene)	1–2.2	No	—	—	Yes	—	—	5-fold	[9]
Drag reducing agent (DRA) poly-α-olefin	0.5	24.5 wt% of hexane	Yes	Yes	Yes	3-fold	9-fold	23–30-fold	[82, 83]
Poly(dimethyl siloxane)	2	No	Yes	Yes	Yes	1.2-fold	2-fold	4-fold	[82, 83]
Tri-n-butyl tin fluoride	1	No	Yes	Yes	Yes	1.5–4-fold	40-fold	60-fold	[82, 88]
Hydroxyaluminum di-2-ethylhexanoate (HAD2EH)	0.5–1	No	No	Yes	Yes	No	10-fold	14-fold	[82, 88, 89]
Cross-linked phosphate esters (HGA 70-C6) + HGA 65	0.25–1	No	Yes	Yes	Yes	1.45-fold	2.6-fold	3.5-fold	[88]

Table 2.
Outline of the solubility in NGL compounds and NGL thickening capability of polymers and small-molecule compounds.

In propane and butane, PDMS was soluble at pressures close to the vapour pressures of propane and butane, while in ethane, it required high pressure (much greater than its vapour pressure) to attain solubility. For example, at 333 K and 2 wt% of PDMS in ethane, propane, and butane, the cloud point pressures were obtained to be equal to 18, 2.56, and 0.92 MPa, respectively. Furthermore, they found PDMS to be an effective thickener in propane and butane but an ineffective thickener in ethane. For example, at 333 K and at a concentration of 2 wt%, PDMS achieved viscosity increases of 1.2-fold in ethane, 2-fold in propane, and 4-fold in butane. It was also found to be a better thickener at high pressure (62 MPa). Overall, high molecular weight PDMS is not a viable thickener of NGL for EOR applications [83].

In comparison to the results obtained by Heller et al. for 2.2 wt% of PAO (poly(1-pentene), poly (1-hexene), and P-1-D) in butane at 298 K, DRA increases butane viscosity substantially at even lower concentrations (0.5 wt%), because of the extremely high molecular weight of DRA, regardless the relatively high concentration of hexane added to the system. Although PDMS has a higher molecular weight (Mw: 980,000 g.mol^{-1}) than PAO, PDMS offers a lower relative viscosity (fourfold) than the viscosity obtained by low molecular weight PAO (fivefold). These observations indicate that the increase in gas viscosity depends on several factors and not solely on the molecular weight of the additives. Additional factors that can influence the viscosity-enhancing ability of an additive include the nature of additives and the solvent, the concentration of additives, the molecular weight distribution of the additives, and the type of intermolecular interactions among the additives and the solvent [84, 85]. These chemical additives (PDMS and PAO) have different chemical structures. PAO has a carbon-carbon backbone with atactic molecular structure of mostly uniform head-to-tail connections with some head-to-head-type connections in the structure [86]. On the other hand, PDMS has silicone-oxygen backbone and more flexible molecules than P-1-D molecules. Hence, PDMS can have lower steric hindrance and greater bond angle (143° vs. 110° for C-C-C) to rotate around the Si-O bond [87]. Furthermore, the effect of molecular structure and polymer molecular weight on viscosity has been studied by Zolper et al. [87] who found that similar viscosity can be obtained for different molecular mass. For example, the viscosity of PAO at 1000 g.mol^{-1} is equivalent to the viscosity of PDMS at around 10,000 g/mol. This was attributed to the additional attractive intermolecular forces between the polymers with increasing branches, which leads PAO to having higher viscosity indices than PDMS. Therefore, the effect of PAO on butane viscosity could be attributed to the structure of the polymer. These effects are more pronounced in improving the solvent viscosity than the PAO molecular weight.

3.2 Small-molecule self-associating thickeners

Similarly to studies for CO_2, low molecular weight self-associating compounds have been studied as thickening agents of light alkane gases for gas mobility control and hydraulic fracturing purposes [54, 82, 88, 89]. Ideally, small-molecule compounds need two processes to attain dissolution and viscosity enhancement [88, 89]. The first is a high-pressure heating cycle, which disrupts the intermolecular association to enhance the dissolution. The second process is the cooling cycle to re-establish the intermolecular association necessary for viscosity enhancement. However, some small-molecule compounds do not require this two-step process to attain dissolution and viscosity enhancement in NGL [89]. Previous studies on the application of small-molecule compounds to increase the viscosity of light alkane gases are discussed in the following section.

3.2.1 Trialkyltin fluorides

Dunn and Oldfield first reported on the use of tri-n-butyl tin fluoride (TBTF) as a direct thickener of non-polar solvents including carbon tetrachloride and n-propane [89]. **Figure 8** illustrates the association mechanism of tributyltin fluoride [90], where a linear polymeric chain of penta-coordinate tin atoms are linked by fluorine atoms. TBTF is a white powder with a melting point of 544 K [88, 89]. The three butyl arms attached to the tin atom enhances the solubility of TBTF in a hydrocarbon solvent, while the intermolecular association formed among the tin and fluorine atoms induces the viscosity-enhancing effect. It has been found that TBTF is soluble in organic liquids and light alkanes under stirring for several minutes without requiring a heating and/or a cooling cycle [89]. TBTF is an effective thickener for intermediate hydrocarbon components. Dandge et al. [54] found TBTF to be capable of improving the viscosity of propane and butane. For instance, at concentrations of 0.13–0.15 wt% at 298 K, it increased the viscosity of these components by 2–10-fold at 8.3 MPa. In addition, they also found that TBTF was only partially soluble in ethane and with no measurable viscosity change [79]. Later on, Enick and co-workers confirmed the ability of TBTF to thicken propane and butane liquids at 298 K at concentrations of 0.2–5 wt% [56]. Other trialkyltin fluorides have been tested in hydrocarbon solvents. Tripropyltin fluoride (TPTF) is not soluble in propane and butane, because the propyl arms are too short to induce the dissolution of TPTF in these solvents [91]. Therefore, it confirms that the solubility of trialkyltin fluoride in n-alkane increases as the number of carbon atoms in n-alkyl arms (R) increases [54]. However, at equivalent mass concentration, TBTF in n-hexane or n-butane has shown to outperform in viscosity enhancement compared with other solvents [54]. For example, at a concentration of 10 g/L and 310 K, TBTF increases the viscosity of n-hexane by 750-fold (from 0.265 cP to 196 cP), while the tetrachloroethylene viscosity is enhanced by 380-fold (124.45 cP) [54].

A recent study has tested the solubility and viscosity enhancement ability for dilute concentrations (>1 wt%) of TBTF in ethane, propane, and butane at high pressures (38–64 MPa) and high temperatures (298–373 K) [82, 88, 89]. TBTF is soluble in propane and butane above the corresponding vapour pressure of these components, while in ethane, TBTF is soluble at much higher pressures than the ethane vapour pressure. In addition, it was observed that the relative viscosity of TBTF in NGL components increases slightly with increasing pressure at all temperatures and TBTF concentrations. Increasing the pressure does not affect the self-assembly of the supramolecular structure; it only affects the solvent strength which has a less significant effect on the solution viscosity. Furthermore, as temperature increases, the intermolecular association between the tin and fluoride
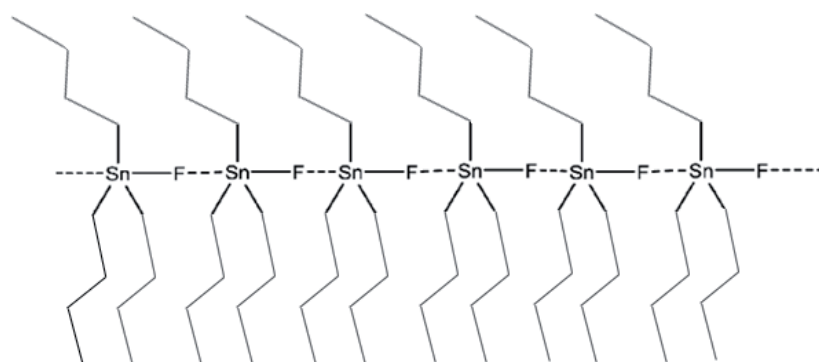
Figure 8.
Association mechanism of tributyltin fluoride [89].

molecules diminish, leading to a significant decrease in the viscosity enhancement in all light alkane components. For example, with 1 wt% concentration of TBTF in ethane at 298 K and 62 MPa, the achieved relative viscosity is 90, and it drops to 75 at 313 K. The relative viscosity significantly drops further to 20, 6, and 1.5 at 333, 353, and 373 K, respectively [82] (**Table 2**).

3.2.2 Hydroxyaluminum di-2-ethylhexanoate (HAD2EH)

A mixture of aluminium disoap and gasoline liquid is heated to high temperatures (368–373 K) to promote its dissolution by dismantling the intermolecular associations between the aluminium disoaps. Then it is cooled down to allow self-assembly of the disoap molecules, whereby the viscosity of the solution is enhanced significantly [88, 89]. Enick and co-workers [62] studied a single aluminium salt, referred to as hydroxyaluminum di-2-ethylhexanoate (HAD2EH). **Figure 9** depicted the association mechanism of HAD2EH. They found HAD2EH to exhibit a remarkable solubility in light hydrocarbon gases such as propane and butane. It is also capable of thickening these components at dilute concentrations. For example, at 293 K, HAD2EH concentrations in the range of 0.2–1 wt% were capable of increasing the viscosity of the solution by 10–100-fold as tested in a high-pressure falling-ball cylinder viscometer. However, the solution formed was hazy, due to a portion of the HAD2EH molecules forming solid fibres in both liquid propane and butane at high pressures.
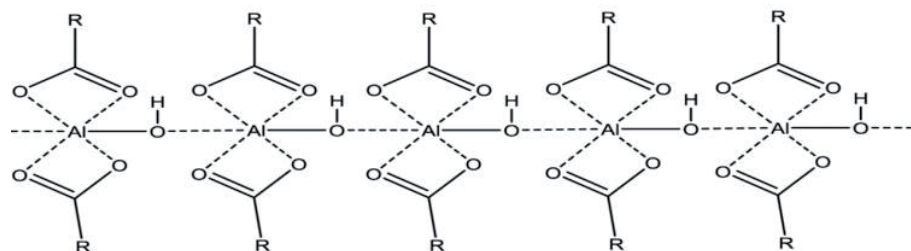

Figure 9.
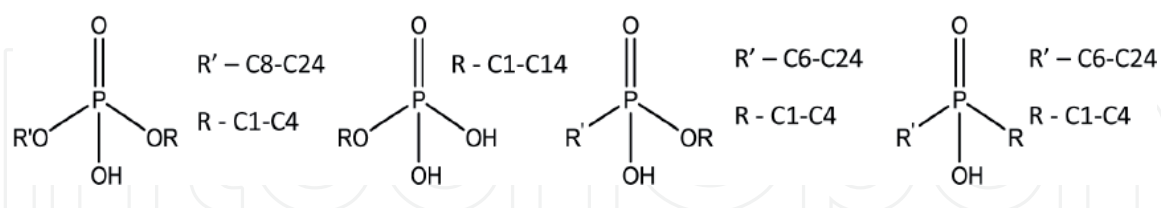*Association mechanism of HAD2EH molecules [89].*

Figure 10.
Molecular structure of phosphate di-/monoester, phosphonic acid ester, and dialkyl phosphinic acid [89].
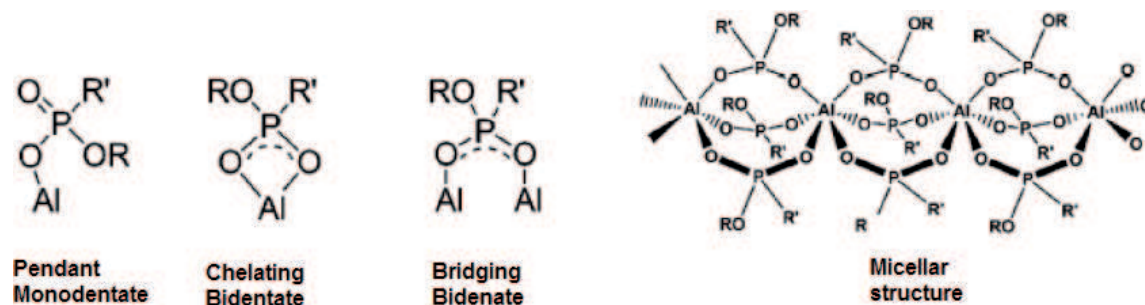

Figure 11.
Chelation mechanism and micellar structure of phosphate ester/metal ion complex [96].

Dhuwe et al. [82, 89] examined blends of HAD2EH in several NGL (i.e. ethane, propane, and butane) individually under a range of pressures (34–62 MPa) and temperatures (298–273 K). HAD2EH was soluble in propane and butane while insoluble in ethane. At a temperature of 298 K, HAD2EH was insoluble in all light alkanes. Heating to 373 K, high pressure, and stirring were required to attain dissolution, followed by cooling to a temperature above 313 K to obtain a single phase solution. If the solution is cooled down to a temperature of 298 K, HAD2EH precipitated in both propane and ethane. Accordingly, it was observed that HAD2EH was an effective thickener in butane and propane at temperatures as low as 313 K. For example, at a concentration of 0.5 wt% HAD2EH and temperatures of 333–373 K, butane viscosity increases by 15–19-fold, while propane is thickened by 2–3-fold [82, 89].

3.2.3 Cross-linked phosphate esters

Several studies report the attempts made to gel light hydrocarbon gas (LPG) using phosphorus-based esters cross-linked with polyvalent metal ions (**Figure 10**) for dry hydraulic fracturing applications [90, 92–95]. These techniques use phosphate mono-/diesters linked to alkyl tails. Typically, a hydrocarbon liquid agent solution is formed by combining two low-viscosity liquid reactants (i.e. a solution containing the phosphate ester and one containing a polyvalent metal ion cross-linking agent) together in the fluid that is being thickened. The two low-viscosity liquids quickly dissolve in the hydrocarbon fluid (e.g. light alkane) without the need of heating and/or cooling cycles. The polyvalent metal ion bound more tightly to phosphate esters than to the ligand, which leads the phosphate ester to quickly chelate with metal ion and form long micellar and a supramolecular structure as shown in **Figure 11**. If this long micellar structure remains soluble in the solvent, then it can significantly improve the solution viscosity. Rapid dissolution of the phosphate ester system in the solvent and the rapid viscosity enhancement kinetics could make these molecular structures attractive for use with NGL in EOR applications [88, 89].

There are a few studies reporting the use of oil-soluble phosphate mono-/diesters, dialkyl phosphinic acids, or alkyl phosphonic acid ester cross-linked with polyvalent metal ions including Fe^{3+}, Mg^{2+}, Al^{3+}, Zn^{2+}, and Ti^{4+} at concentrations of 0.2–2.5 wt% to increase the viscosity of hydrocarbon oils (e.g. diesel and kerosene) by 2–100-fold [93, 94, 97]. Furthermore, phosphate-based esters could be used as gel agents for CO_2 and hydrocarbon liquid mixtures [98, 99]. Lee and Dhuwe et al. [82, 88, 89] studied blends of cross-linked phosphate esters (CPE) (phosphate ester (HGA 70-C6) and cross-linker (HGA 65)) with NGL components (ethane, propane, and butane) at temperatures ranging from 298 to 373 K and pressures ranging from 13.8 to 62 MPa. They found that phosphate ester and the cross-linked solution are soluble in ethane, propane, and butane at concentrations of 0.25–1 wt% and temperatures of 298–333 K. However, the cross-linked solution was slightly hazy due to small droplets of CPE suspended in the solution. This mixture (phosphate ester + cross-linker) achieved a modest viscosity increase in ethane, while greater increases occurred in propane and butane. For example, at a concentration of 1 wt% at 333 K and 20.68 MPa, the viscosity of ethane increased by a factor of 1.45-fold, and the viscosity of propane and butane increased by 2.6- and 3.2-fold, respectively. This mixture cannot form a single phase in the NGL components due to the suspension of very small droplets of CPE in the solution and because its suitability for injection into porous media is limited [88] (**Table 2**).

4. Conclusion

Despite of over five decades of extensive work in developing and identifying viable gas thickeners for EOR applications such as fluorous and non-fluorous polymers, copolymers, and low molecular weight compounds, so far none of these materials may be considered effective thickeners for field applications [6]. In fact, the design of affordable thickeners for CO_2 or HC gases effective at low concentrations (i.e. <1 wt%) is highly challenging due the low solubility of the additives in these solvents.

The main conclusions derived from this review are as follows:

- At laboratory scale, the best CO_2 thickeners are PDMS, P-1-D, polyFAST, and PFOA for CO_2 mobility and conformance control. However, the use of these materials for field applications is not sustainable due to their elevated manufacturing costs, the large concentrations required to ensure technical success, and environmental concerns.

- There are several small-molecule compounds that have been identified as CO_2 thickeners including semi-fluorinated trialkyltin fluorides, fluorinated bis-ureas, di-chain perfluorinated sulphosuccinate surfactants, and branched benzene trisurea. In general, these compounds are capable of increasing the CO_2 viscosity between 1.5- and 300-fold at lower temperatures (298–313 K). However, most of these materials are fluorinated and can improve the viscosity only at high concentrations (2–10 wt%). In addition, the intermolecular associations displayed by these compounds are effective at low temperatures; therefore, they cannot be used at typical reservoir conditions due to the diminishing intermolecular associations at high temperature [2].

- Effective polymer thickeners for NGL components include DRA polymers, PDMS, and PAO oligomers. These polymers are much more effective for thickening butane and less effective for propane and ethane. DRA polymers are promising thickeners (3–23-fold) at dilute concentrations over temperatures of 298–333 K, while PDMS and PAO show moderate viscosity enhancements (1.2–5-fold) over the same temperatures. In addition, P-1-D seems to be a suitable thickener in an AG mixture at temperatures above 373 K.

- Small-molecule compounds such as TBTF, HAD2EH, and CPE are effective thickeners for pure light alkane components at moderate temperatures (313–333 K). Nevertheless, phase behaviour and environmental issues (fluorine content) prevent the use of these materials for EOR applications.

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