A Literature Review of Attempts to Increase the Viscosity of Dense Carbon Dioxide

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ABSTRACT

Two important processes in the oil and gas industry that use dense carbon dioxide are fracture stimulation and enhanced oil recovery. For enhanced oil recovery, the problems with using carbon dioxide have been well studied and documented in laboratory and field studies. The low viscosity of carbon dioxide causes it to 'finger' towards the production wells and bypass large amounts of oil. Significant research has been conducted over the past 15 years searching for ways to increase the viscosity of (thicken) carbon dioxide.

Because of the low viscosity of dense carbon dioxide, its effectiveness as a fracturing fluid has been questioned. Specifically, the effect of low fluid viscosity on proppant settling, placement of high sand concentration, and fluid leakoff is poorly understood. Nonetheless, Canadian Fracmaster has fracture stimulated thousands of wells in Canada via CO_2-sand fracturing (100% carbon dioxide and proppant) with great success. The U.S. Department of Energy has several initiatives to introduce CO_2-sand fracturing in the U.S. and demonstate its applicability as a non-damaging fracture stimulation technique. Although most of the fracture stimulations have led to increased production/deliverability, the above questions with respect to the low viscosity still remain. This may in part be due to the trend over the last 7 years or more in the oil and gas industry to use high viscosity fluids, e.g. linear gels and cross-linked gels, for better fluid leakoff control and placement of higher sand concentrations. With the huge difference in viscosity between dense carbon dioxide and gelled fluids, an increase in the viscosity of carbon dioxide could improve the placement of more and larger sand particles and improve fluid leakoff. Hence the objective of this study was to review all previous and current research in the area of carbon dioxide viscosity enhancement and provide assessments of future research directions with respect to increasing the viscosity of carbon dioxide for CO_2-sand fracturing. Ideally, the viscosity of carbon dioxide could be increased by a factor of 2-100 and the compound(s) used would be non-damaging to the formation (i.e., they would either be produced back with the gaseous carbon dioxide or be of such small quantity that porosity and permeability of the formation and proppant pack would not be reduced).

The goal of most research efforts was to increase the viscosity of dense carbon dioxide via the dissolution of dilute concentrations (less than 1 wt. %) of 'thickeners'. This review has indicated that three basic strategies have been followed. In the first, extremely high molecular weight polymers were considered. These compounds were either insoluble or sparingly soluble in carbon dioxide unless prohibitive amounts of co-solvent were added. In the second

strategy, relatively low molecular weight compounds capable of forming viscosity-enhancing pseudo-networks of polymers via associations, hydrogen-bonding, or micelle formation were evaluated. These compounds contain polar groups that diminish carbon dioxide solubility. Hence, large amounts of co-solvent were required to enhance their CO_2-solubility in order to increase viscosity. The third group of studies included recent efforts to design novel viscosity enhancing molecules that exhibit very high carbon dioxide solubility. One high-molecular weight CO_2-thickening polymer, a poly fluoroacrylate, and one low MW associative thickener, a fluoroether disulfate telechelic ionomer, have been identified. Both can increase the viscosity of carbon dioxide in concentrations of several weight percent without the need for a cosolvent, but they are synthesized using expensive, highly fluorinated precursors.

Efforts to reduce the apparent viscosity of carbon dioxide mobility via non-aqueous emulsions (droplets of liquid carbon dioxide separated by films of an immiscible aqueous or oleic liquid) were also reviewed. For example, attempts have been made to develop emulsions that are about 95-98 vol% or more liquid carbon dioxide and 2-5 vol% non-aqueous films (unlike miscible displacement, water cannot be used in fracturing applications because the CO_2 is injected at temperatures well below the freezing point of water). These emulsions are relatively difficult to stabilize due to the difficulty in identifying effective surfactants for mixture of non-polar liquids. A limited amount of promising results were published, however.

Several research groups continue to search for an effective carbon dioxide thickening agent. Their efforts continue to focus on (1) inexpensive thickening agents that require large volumes of co-solvents (e.g. 2 vol% thickener, 15% toluene, 83%carbon dioxide) or (2) expensive thickeners based on silicone-based or fluorine-based compounds designed to exhibit high carbon dioxide-solubility without any co-solvent. In the near-term, neither of these efforts is likely to provide an economically viable method for enhancing the performance of CO_2. In the long term, however, these efforts may yield economic thickeners that require little or no co-solvent.

The use of non-aqueous emulsions may still be a viable option because very small amounts of the non-aqueous phase are required (e.g. 1/10th to 1/50th the amount of liquid carbon dioxide). Further, small amounts of surfactants are required to stabilize the emulsion (e.g. 1/100 of the non-aqueous phase). Much progress has been made in the 1990's in surfactant development for chemical engineering processes employing liquid CO_2. Although these surfactants are expensive because they are based on silicones or fluorinated functionalities, they would be required in very small amounts. A substantial portion of the surfactant and non-aqueous fluid would probably remain within the fracture and formation upon depressurization because of their low solubility in natural gas. Therefore, the benefits of the increased viscosity of the carbon dioxide would possibly be mitigated by the potential formation damage caused by these residual fluids.

TABLE OF CONTENTS

I. THE NEED FOR ENHANCED CARBON DIOXIDE VISCOSITY

1.0 Technical Issues and Objectives

1.1. Carbon Dioxide Miscible Displacement

Carbon dioxide can be injected into an oil reservoir to recover oil left behind during waterflooding. This enhanced oil recovery technique is commonly referred to as carbon dioxide miscible displacement (1). During a miscible displacement project, carbon dioxide dynamically develops miscibility as it mixes with the oil in the porous media. This process is conducted at or slightly above the 'minimum miscibility pressure' to ensure that the solvent strength of the CO_2 is great enough to attain a high degree of solvency for the oil that it contacts. As the reservoir fluids are produced from the reservoir, the carbon dioxide can be readily separated from the oil and brine via pressure reduction. The availability of large volumes of low cost carbon dioxide, along with its low-toxicity, non-flammability and classification as a non-VOC combine to make it an attractive fluid for EOR.

Carbon dioxide enters the oil-bearing porous media at reservoir temperature, which is usually between 80ºF and 250ºF. The CO_2 is introduced at a pressure that is high enough to enable miscible displacement to be achieved, referred to as the minimum miscibility pressure, MMP. Over 15 correlations for the MMP have been developed, with several examples illustrated in Figure 1. The foremost disadvantage of CO_2 as a oil displacement fluid is its low viscosity, 0.03-0.10 cp at these reservoir conditions, as shown in Figure 2. The brine in a reservoir has a viscosity on the order of 1 cp, while the reservoir oil viscosity varies between 0.1 - 50 cp. The CO_2 slug therefore has a much higher mobility (the ratio of a fluid permeability in porous media to viscosity) than the fluid it is displacing, resulting in an unfavorably low mobility ratio (the ratio of the CO_2 mobility to the fluid it is displacing is much less than unity). As a result, the areal sweep efficiency of the flood can be very low as the CO_2 'fingers' toward the production wells rather than uniformly displacing the oil ahead of it toward the production wells. Even though the displacement efficiency of the CO_2 may be very high *for the oil it contacts*, these fingers result in the CO_2 *bypassing much of the oil* in the reservoir. Consequently, if the carbon dioxide viscosity could be elevated to a level comparable with the oil it is displacing, typically a 1-2 order of magnitude increase, substantial improvements in sweep efficiency and oil recovery could result.

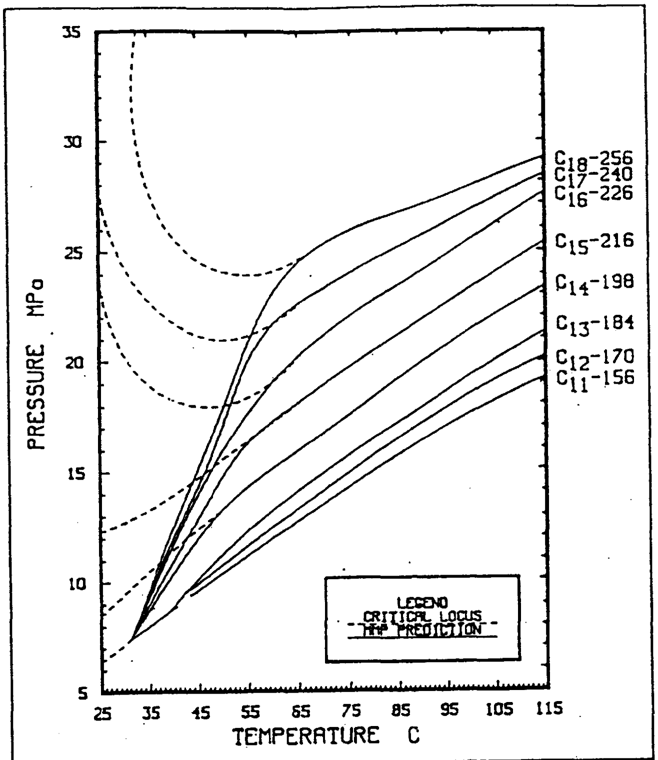


Fig. 4—MMP correlation—pure CO_2/stock-tank oil.

TABLE A-1—NATL. PETROLEUM COUNCIL MMP CORRELATION

Gravity (°API)	MMP (psi)
<27	4,000
27 to 30	3,000
>30	1,200

Reservoir Temperature Correction

T (°F)	Additional Pressure (psi)
<120	0
120 to 150	+200
150 to 200	+350
200 to 250	+500

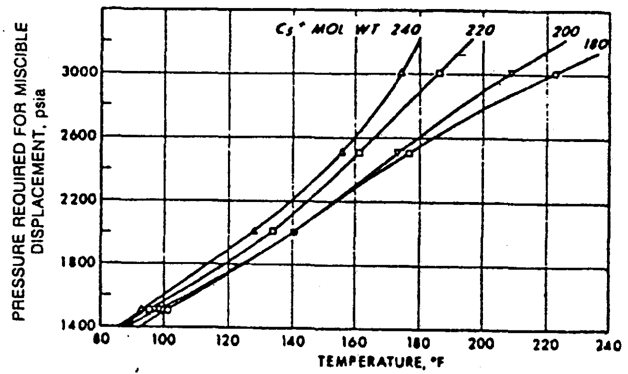


Fig. A-1—Holm and Josendal[2] correlation for predicting pressure required for miscible displacement in CO_2 flooding (after Benham *et al.*[8] for a 59% methane/41% propane displacing fluid).

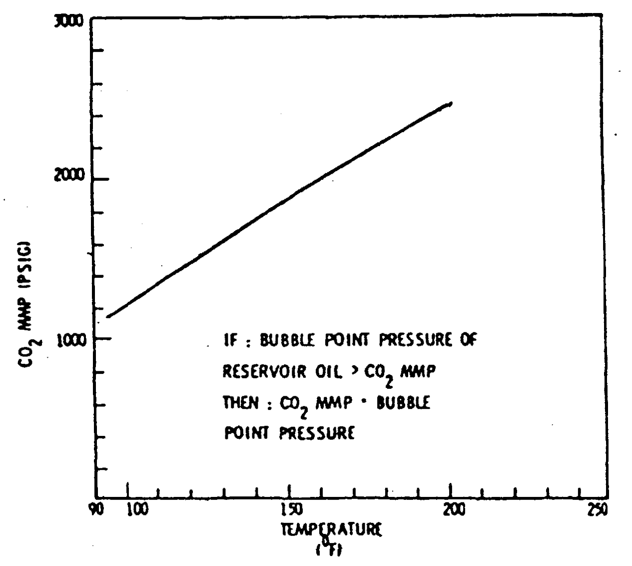


Fig. A-3—Yellig and Metcalfe[3] correlation.

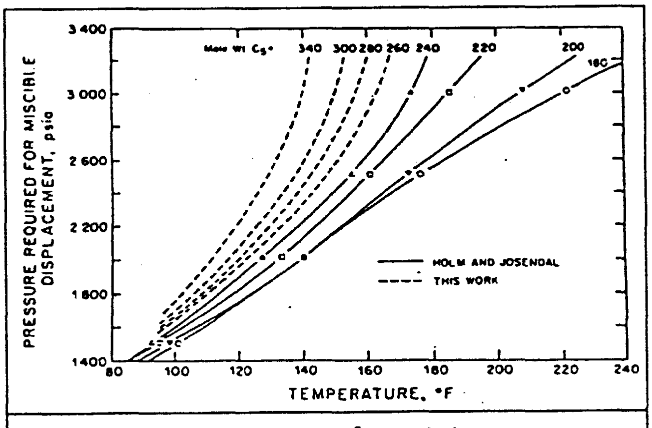


Fig. A-2—Mungan[5] correlation.

Figure 1. Examples of MMP correlations for Carbon Dioxide Flooding, from a review paper (Reference 2)

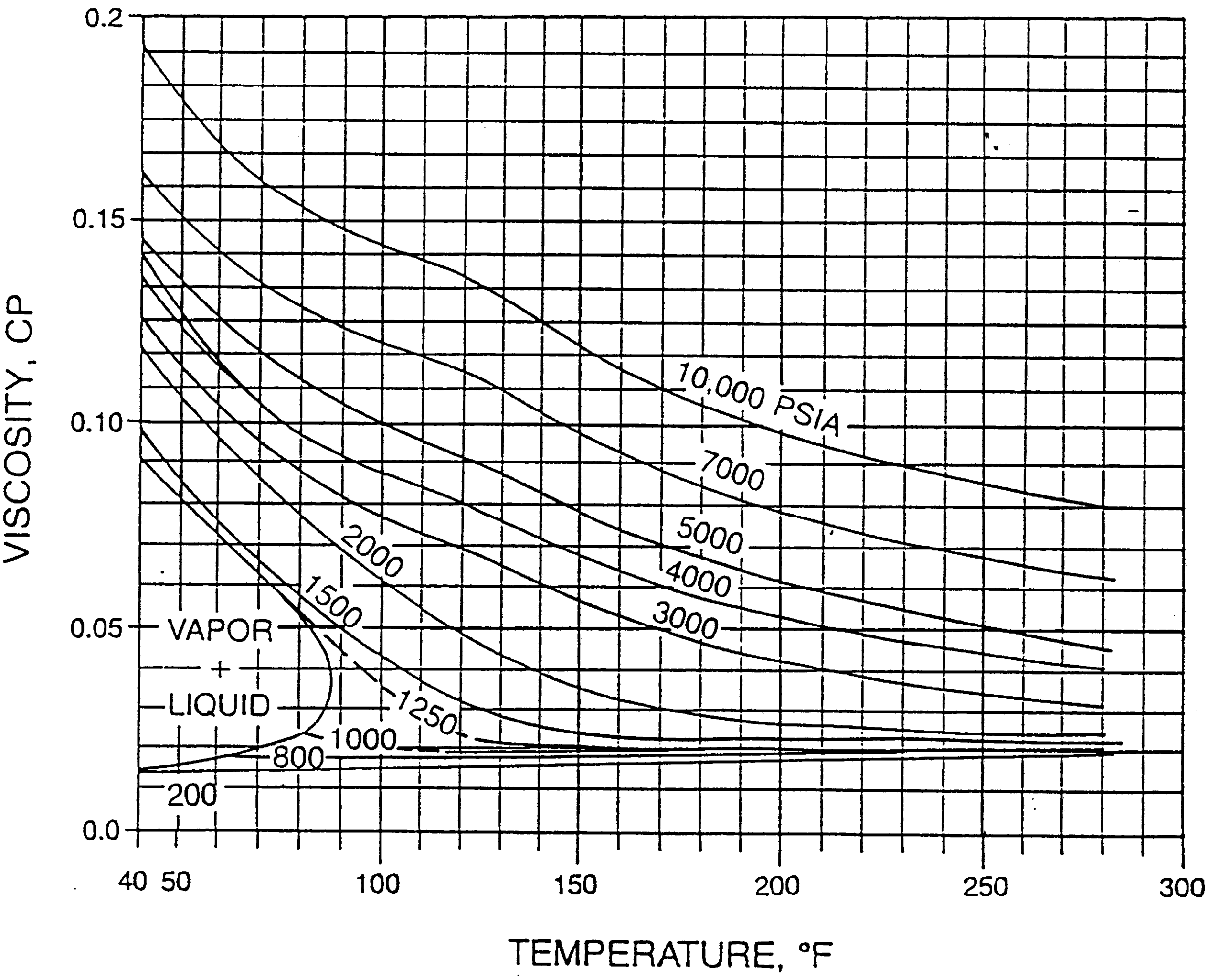


Figure 2. Viscosity of Carbon Dioxide as a Function of Temperature and Pressure

The low viscosity of CO_2 also reduces oil recovery in stratified reservoirs, where the high mobility of CO_2 induces it to preferentially enter highly permeable zones. Oil residing in less permeable layers will not be displaced efficiently because only a small portion of the CO_2 injected into the well will enter these layers. A reduction in CO_2 mobility would tend to mitigate this effect, although profile modification (reducing the permeability of the high-perm zones, thereby redirecting injected CO_2 to the lower-perm layers) of stratified reservoirs is a more effective means of addressing this problem.

1.2. Fracturing Formations with Liquid Carbon Dioxide

Another petroleum engineering technology that employs dense carbon dioxide is the fracturing of gas and oil wells (2-11). CO_2-rich mixtures have been used for fracture cleanup and sand fracturing of wells since the early 1960's, with the sand being carried by a second phase, such as gelled water, methanol, or oil. The use of liquid CO_2 as the only constituent of a fracturing fluid has been employed since the early 1980's. Recently, CO_2-N_2 mixtures have also been employed. The fracture is generated by the pressurized fluid and is then propped open by the sand particles. The CO_2 is then removed through the wellbore when it is opened to flow for production. The productivity of the frac is optimized when the fracture penetrates deeply within the formation and is efficiently propped without damaging the reservoir. The high solubility of CO_2 in oil, its miscibility with natural gas, its high vapor pressure, and its ability to eliminate permeabilty damage around the frac result in the elimination of residual fluid left in the formation, rapid cleanup, and low cost. The carbonic acid that forms in reservoir water (pH = 3-4) in the presence of dense carbon dioxide has not been known to damage sandstone formations. The pressure-temperature path taken during a typical frac job is illustrated in Figure 3. The carbon dioxide is in the liquid or liquid-like density supercritical phase during the frac, expanding to gas-like conditions only when produced through the well.

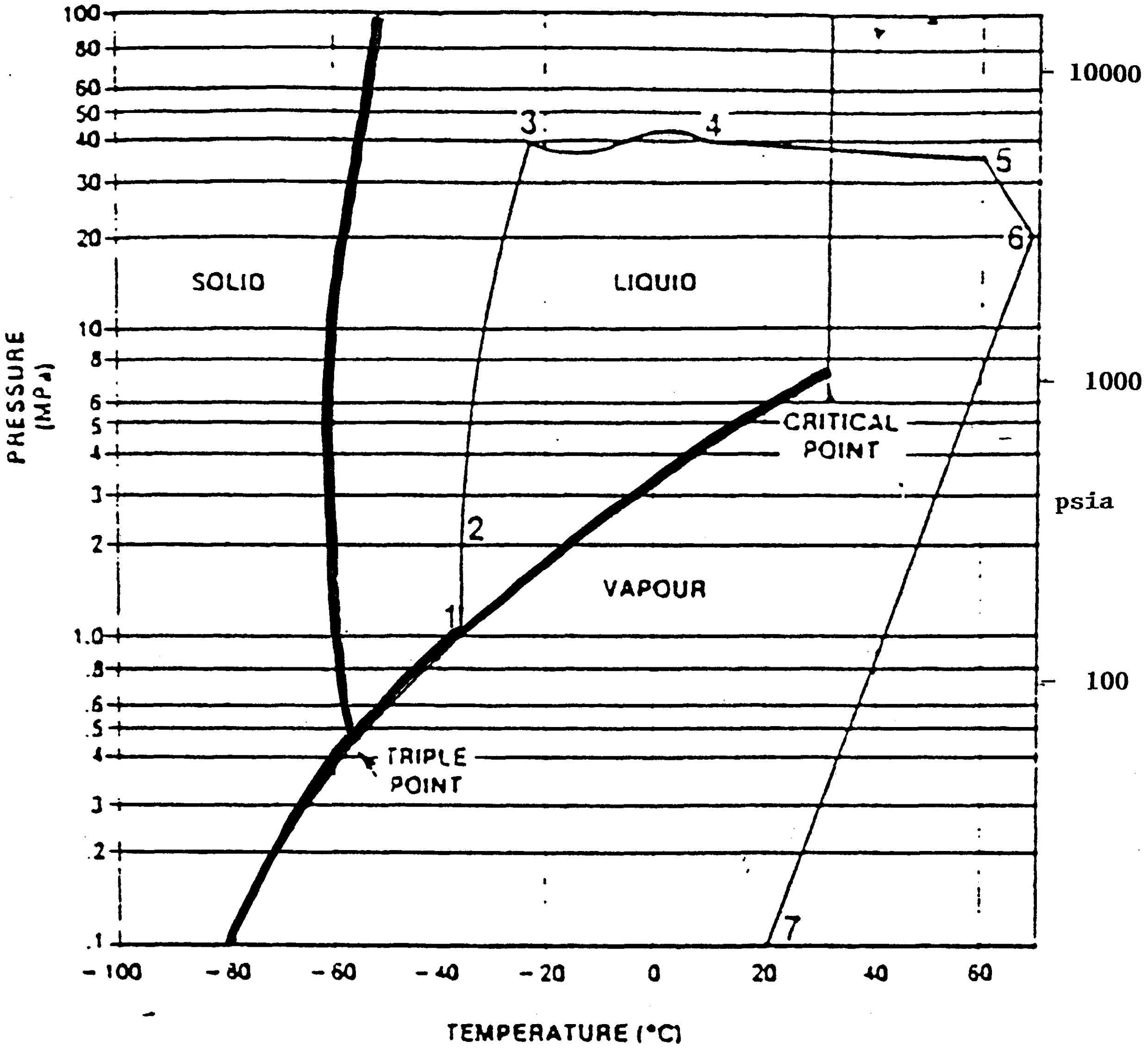
CO_2 would probably be an even more effective fracturing fluid if its viscosity was increased. There are three aspects of fracturing that may be influenced by the viscosity of carbon dioxide.

After the sand has been carried into the fracture by the carbon dioxide and the carbon dioxide injection has ceased, the sand will rapidly settle in the fracture. As a result lower sand concentrations and smaller sand sizes must be used. For example, 40/60 mesh sand may have to be used with carbon dioxide, rather than the 20/40 mesh sand used with conventional fluids. A more viscous carbon dioxide may enable more sand of larger size to be distributed more uniformly when the fracture closes on the proppant particles.

Fluid leak-off is also high due to the low viscosity of carbon dioxide, making it less effective in high-permeabilty reservoirs. The leakoff rate for carbon dioxide into the formation will also be reduced if the viscosity of the carbon dioxide is increased.

The increase in carbon dioxide viscosity will decrease the Reynolds number of the flow through the fracture (flow through a slot). If the carbon dioxide flow through the fracture is transitional or in the low Reynolds number range of turbulent flow, a significant increase in the carbon dioxide viscosity will result in the flow changing from the turbulent or transition regime to laminar flow. Because a significant *decrease* in the friction factor would accompany this change, the net pressure would decrease and the fracture width would decrease. It is also believed that the proppant carrying capacity of carbon dioxide would be reduced. Therefore the viscosified carbon dioxide could *diminish* the fracture's productivity. If the flow of carbon dioxide in the fracture was laminar or fully turbulent, the viscous carbon dioxide would decrease the Reynolds number but not change the flow regime. This would increase the friction factor, thereby *increasing* the fracture width.

Even if the CO_2 could be thickened and the fracture productivity increased, the effects of the thickener itself should be considered. Dilute concentrations of the thickener must be employed because the thickening agent may precipitate within the fracture upon depressurization, especially if it is a solid or viscous liquid that is not soluble in the gas or oil flowing from the reservoir. Therefore the increased productivity of the more extensive fracture would be mitigated by formation damage caused by precipitation of the thickening agent.



1 - Lease tank conditions

2 - Pressure boost prior toblender injection

3 - Pressurization to wellhead conditions

4 - Perforation condition

5 - Frac-tip conditions

6 - Shut-in condition, warming to reservoir temperature

7 - CO_2 expansion as well is opened to flow

Figure 3. Typical PT Path for CO_2 During a Frac Job (Reference 6)

1.3. Previous Attempts to Decrease the Mobility of Carbon Dioxide

The efficiency of both carbon dioxide miscible displacement and carbon dioxide fracturing can be improved if the mobility of dense CO_2 can be decreased. There have been three methods of approaching this problem, (1) reduction of CO_2 relative permeability in the reservoir via co-injection with water, (2) generation of a CO_2 foam, and (3) increasing the viscosity of CO_2 via the addition of a 'thickening agent'.

1.3.a. Reduction in Relative Permeability via Water Injection for Mobility Control

The initial attempts to diminish CO_2 mobility (the ratio of fluid permeability to viscosity) for miscible displacement were focused on the reduction of the relative permeability of the CO_2, rather than increasing its viscosity. This permeability reduction was accomplished by injecting water simultaneously or alternately with the carbon dioxide (12-13), thus diminishing the CO_2 saturation within the porous medium (thereby lowering its relative permeability). Although some success was realized with this technique, new problems were also encountered. These included the increased amount of time required to inject the required volume of CO_2 and the 'shielding' of oil by high water saturations in the porous media that inhibited the mixing of the oil and the CO_2.

1.3.b. CO_2-Foams for Profile Modification, Mobility Control, and Fracturing

Several teams of researchers have investigated the use of CO_2-foams (also referred to as emulsions) for mobility control or for blocking high-permeability zones (14-16). Foams can be formed by injecting an aqueous surfactant solution into the reservoir. Subsequently, a CO_2 slug is injected. As the CO_2 is injected, foam will be generated in-situ. The CO_2 resides inside 'bubbles' that are separated by thin aqueous films. Because most of the aqueous solution will enter the most permeable zone, these foams will form in the high permeability zones upon the CO_2 injection. Tremendous reductions in CO_2 mobility can occur when these foams form and thus these foams can be used for profile modification to block preferential flow channels caused by reservoir heterogeneities. These foams can also improve mobility control if the mobility reduction realized upon their formation can be moderated. This may occur as the surfactant adsorbs and the foam breaks down when it contacts oil as it propagates through the reservoir. A recent field test of CO_2 foams (9) has demonstrated both profile modification and mobility control.

Canadian Fracmaster - 1982-1987

*CO_2 foams with a non-aqueous liquid as the continuous phase and carbon dioxide as the discontinuous phase within the bubbles have been evaluated for the low temperature mobility reduction of CO_2 used for hydraulic fracturing (*2-6*).* This effort represented a two-phase fracturing fluid with the highest possible portion of liquid carbon dioxide and lowest amount of the non-aquesous phase possible. A non-aqueous phase was used rather than water because the temperature of the CO_2 injected into the wellhead (about -20 to -26° C) is well below the freezing point of water. In their first published results on the formation of high phase volume liquid carbon dioxide emulsions, Canadian Fracmaster reported the difficulties associated with forming and stabilizing such systems. They attempted to form emulsions with up to 90 volume % CO_2 using non-aqueous phases such as diesel fuel, hexane-diesel mixtures, methanol, methanol-water, or water-glycerol mixtures. Attempts were made to stabilize these emulsions using one or more commercially available surfactants.

The authors correctly noted in their paper that the foremost difficulty in forming and stabilizing such systems is the identification of an appropriate surfactant. A typical surfactant molecule has two segments, a small polar 'head' group that 'likes' water (hydrophilic) and a larger 'tail' that is attracted to an oil phase rather than water (hydrophobic). These commercial surfactants are designed for systems involving an aqueous phase and an oleic phase. Many other surfactants that contain hydrophilic and hydrophobic segments are suitable for aqueous phase-gas phase foams, or emulsions of a polar oil and a non-polar oil. *The surfactant required for CO_2 -emulsions must contain a segment that 'likes' or readily dissolves in carbon dioxide and a segment that 'likes' a non-aqueous phase such as diesel fuel. Both of these segments would be hydrophobic. None of the currently available surfactants are designed for such an application.* If a CO_2-immiscible oil is desired as the continuous phase of the emulsion (the films/lamellae with carbon dioxide as the discontinuous bubble phase), the surfactant must contain a segment that is *CO_2-philic* and a segment that is oil-philic. *Future research and development efforts should be directed toward the design of new surfactants with these specific characteristics.* Novel surfactants with CO_2-philic segments have recently been developed at the University of

Pittsburgh and the University of North Carolina at Chapel Hill for CO_2-water systems. *These technologies could readily be extended to the design of surfactants for CO_2-diesel fuel emulsions used in well-fracturing.*

In subsequent work, Canadian Fracmaster reported stable emulsions with phase volumes of liquid carbon dioxide as high as 98%. The non-aqueous phase of their emulsion was a mixture of higher molecular weight fatty alcohol, a sorbitan fatty acid ester, and diesel oil. The replacement of a portion of the fatty alcohol with a fatty acid of the same carbon number yielded a more stable, higher viscosity, lower cost emulsion referred to as “2P”. This fluid had a viscosity of 26 cp at -26C. Five successful field applications were noted by the authors. It was not apparent, however, if the results were significantly better than those that would have been obtained using carbon dioxide alone. (Although these systems may have been emulsions, it is also possible to form suspensions of non-aqueous droplets in a continuous liquid phase if the surfactant is absent or ineffective.)

1.3.c. Identification of a Carbon Dioxide Thickening Agent for Mobility Control

Since the early 1980's, several research groups have attempted to identify a CO_2 ‘thickener’ that would induce substantial increases in the viscosity of dense carbon dioxide, while being inexpensive, safe, and stable at reservoir conditions. Further, it would tend to remain in the CO_2-rich phase rather than partitioning into the brine or oil or adsorbing onto the porous media. The level of viscosity increase should be easily controlled via the concentration of the thickening agent, and should not be necessary to inject water with the thickened carbon dioxide, as is done with foams. Carbon dioxide saturation would therefore be higher, resulting in a higher displacement efficiency of the oil, and the corrosive problems associated with the carbonic acid formation in water-carbon dioxide mixtures would be reduced. Ideally, this thickener would increase the viscosity of CO_2 by 1-2 orders of magnitude when present in concentration of one weight percent or less, although smaller increases, such as a 2-10 fold increase, may significantly improve the performance of carbon dioxide fracturing.

Much of the effort to identify this carbon dioxide thickener was centered on compounds known to increase the viscosity of light alkanes such as propane, pentane, hexane or iso-octane. This was attributed to the alleged similarity of the solvent power of these light alkanes with dense carbon dioxide. Liquids such as pentane also facilitated the ambient pressure screening of compounds prior to their evaluation in high pressure carbon dioxide experiments. There was also an interest in identifying thickening agents for LPG, butane, propane, and ethane, because these fluids are excellent solvents for oils and can be used as miscible displacement agents or as fracturing fluids. Although these fluids are stronger solvents for oil than CO_2, their high cost prevents them from realizing the widespread usage associated with carbon dioxide flooding.

NMIMT - Heller and coworkers, 1983-present

Heller and coworkers at the NMIMT studied this problem extensively (17-26). They initially evaluated commercially available polymers in an attempt to enhance the viscosity of dense CO_2 by dissolving a small amount of a high molecular weight polymer. Their results were unsuccessful due to the extremely low solubility of polymers in carbon dioxide as well as the fact that random coil polymers are not efficient viscosity-enhancers when present in dilute concentration. Their goal was to maximize the entropy of mixing between carbon dioxide and polymer (promoting dissolution) via introduction of disorder and irregularity in a multicomponent polymer. Therefore they synthesized amorphous, atactic polymers of various molecular weights with side chains that varied in carbon number. Although slightly soluble in CO_2, these polymers did not induce a significant viscosity increase.

Heller and coworkers also considered the formation of associative pseudo-polymers composed of tri-alkyltin fluorides as a thickener. These compounds form high molecular weight, linear aggregates via transient associations between adjacent molecules when dissolved in non-polar fluids. Although these compounds were successful thickeners for LPG components, they were not soluble enough in CO_2 to cause a viscosity increase.

Heller and coworkers also studied ionomers synthesized from ‘telechelic’ polymers, i.e. polymers that have ionic groups at each end of the chain functionalities at the ends of the polymers. These compounds were hypothesized to be capable of associating to form pseudo-networks in non-polar solvents. These types of compounds can thicken light alkanes, but their ability to enhance the viscosity of CO_2 has not been substantiated, primarily due to the low solubility of functionalized *alkyl-based* ionomers in dense carbon dioxide. (Alkyl-based polymers are insoluble in carbon dioxide, and the addition of polar groups further reduces carbon dioxide solubility.)

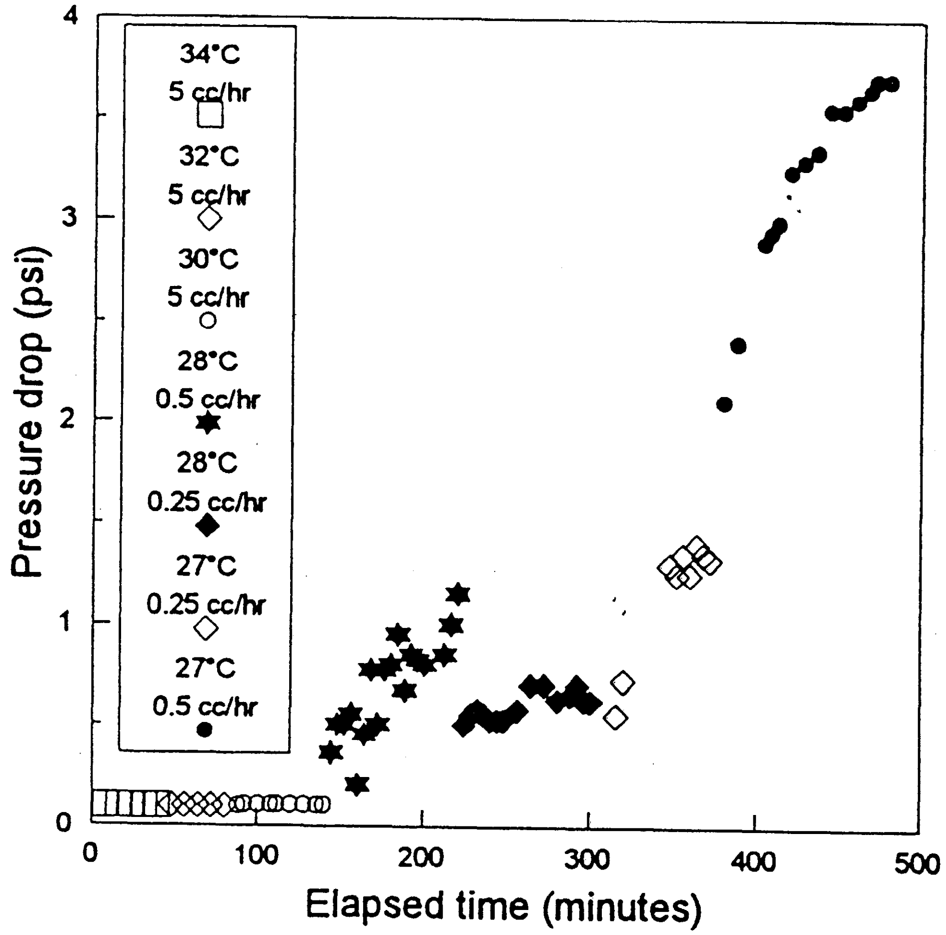
Recently, Heller and co-workers (26) presented the results of their attempts to gel organic fluids and carbon dioxide with 12-hydroxystearic acid, HSA. At a concentration of 0.75 wt%, HSA induced thermoreversible gelation of hydrocarbon and chlorinated liquids. HSA was essentially insoluble in dense carbon dioxide, however. The addition of a significant amount of co-solvent, such as 10-15% ethanol, resulted in the dissolution of HSA and the formation of a translucent or opaque gel phase. The gelation of CO_2 with HSA was found to be a function of temperature, concentration of HSA, and the concentration of ethanol in the dense carbon dioxide. For example, only a slight increase in solution viscosity was observed for a 3% HSA/15% ethanol/82% CO_2 mixture at 34^o C and 1800 psia. A 100-fold increase in viscosity was observed at a slightly lower temperature of $27\text{-}28^o$ C as evidenced by a dramatic increase in the pressure drop of the capillary viscometer, Figure 4.

University of Wyoming - Terry and coworkers, 1987

Terry, et al (27) attempted to increase the viscosity of CO_2 via the in-situ polymerization of CO_2-soluble monomers. They found that polymerizations could be achieved in the high pressure CO_2 environment using commonly available initiators. The alkene monomers selected for this study, ethylene, octene, and decene, were miscible with CO_2 at the test conditions. The hydrocarbon polymers precipitated in the form of a solid phase rather than remaining in solution, however, and thus no changes in solution viscosity were detected.

NIPER - Llave, Chung and Burchfield, 1990

The use of 'entrainers' as CO_2-thickeners was evaluated by NIPER (28). These compounds were relatively low molecular weight, CO_2-soluble compounds such as alcohols, ethoxylated alcohols, and hydrocarbons. Although substantial viscosity increases were reported, such as 243% with isooctane and 1565% with 2-ethylhexanol, the entrainer concentrations were very high, 13 mole% and 44 mole%, respectively. When present in a more dilute concentration, such as 2 mole%, the viscosity enhancement was only 24% for 2-ethylhexanol.



Pressure history of CO_2/15% ethanol/3% HSA during viscosity measurements at 1800 psig

Figure 4. Increase in Viscosity as a Function of Temperature for the CO_2/Ethanol/HSA System

Canadian Fracmaster - 1982-1987

Investigators interested primarily in CO_2 as a fracturing fluid also attempted to enhance the viscosity of dense CO_2 (3-6,9) using direct thickeners. These tests were conducted at a low temperature, -26°C, the delivery temperature of the CO_2 from the trucks which transport the fluid to the wellhead. Compounds known to increase the viscosity of light alkanes, such as polymers and fumed silica, were tested. Reactive systems, including in-situ polymerization of organic/inorganic networks via transition metals and the reaction of CO_2 with amines to form ammonium carbamates (known to gel diesel fuel), were also investigated. None of these attempts were successful, however, due to the very low solubility of these compounds in the CO_2.

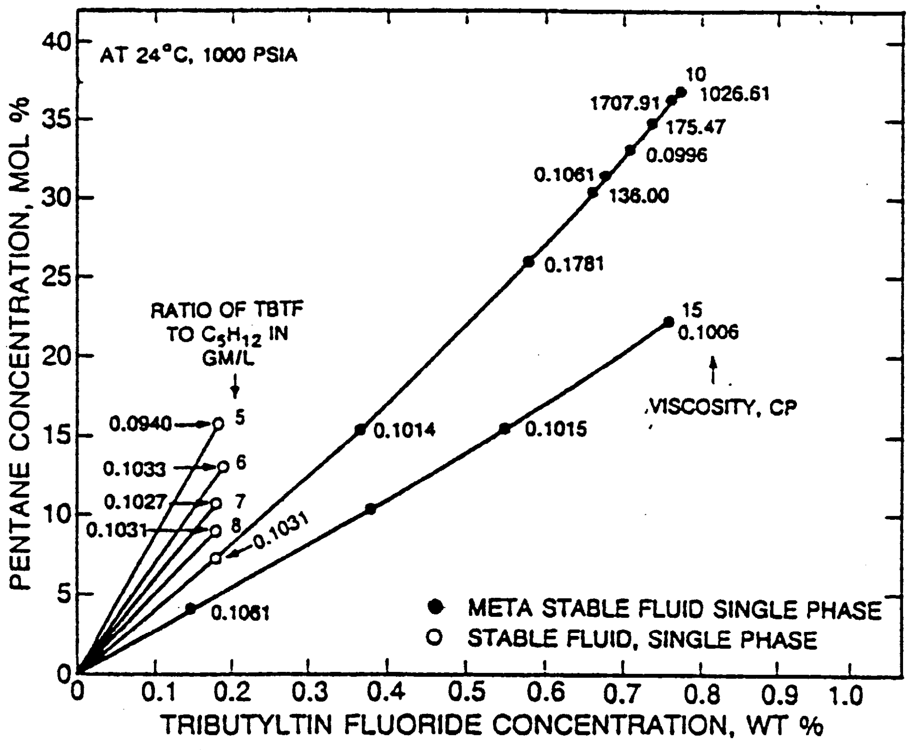
University of Pittsburgh, Enick, Beckman, and coworkers, 1989 - present

Our attempts at the University of Pittsburgh to enhance the viscosity of carbon dioxide (29-36) began with the evaluation of surfactants (amphiphilic compounds containing a hydrophilic head group and a hydrophobic tail). At concentrations above the CMC (critical micelle concentration), these compounds can aggregate as spheres or cylinders. Geometries such as rods or cylinders can lead to substantial increases in solution viscosity. Approximately 80 commercially available oil-soluble surfactants were evaluated in our labs. Surfactants, such as hydroxyaluminum 2-ethylhexanoate, were capable of increasing the viscosity of propane, yet none of the commercially available surfactants were soluble enough in CO_2 to induce a viscosity increase. Other investigators have also reported the extremely low solubility of surfactants in CO_2.

Semifluorinated alkanes, diblock compounds (an alkane segment and a perfluorinated alkane segment) had previously been used to form gels in light alkanes. This occurred when the alkane was heated, dissolving the semifluorinated alkane, and then cooled. Upon cooling, microfibrilles of the semifluorinated alkane formed, which interlocked with the alkane in the voids, forming a ‘gel’. These fibers formed due to the alignment of perfluorinated and hydrocarbon segments. Similar results were obtained when liquid CO_2 was used as the fluid. Because this ‘gel’ was not a single, viscous, transparent fluid phase, but rather a dispersion of carbon dioxide in a network of solid fibers, it was unsuitable for flow in porous media or in fractures.

We also investigated several polymers for their ability to raise the viscosity of dense carbon dioxide. It had been previously reported that CO_2 could be used to fractionate perfluorinated ether oils, such as the Krytox series of oils manufactured by DuPont. The highest molecular weight (13,000) commercially available perfluorinated oil was determined to be *completely miscible with* CO_2 at ambient temperature and a pressure of only 18 MPa (2600 psia). The viscosity increase associated with a 10wt% solution of this polymer in CO_2 was only 8%, however. Fluoroether oils with MW as high as 30,000 were recently evaluated as carbon dioxide-thickeners, but no substantial improvements were achieved at concentrations of several weight percent. Using a fluoroether diol and a fluoroether di-isocyanate, we generated a cross-linked fluoroether-based polyurethane in CO_2. Although the resultant polymer was soluble to 4 wt% in dense carbon dioxide, only marginal increases in CO_2 viscosity were observed.

Light alkane co-solvents were used to enhance the solubility of tributyltin fluoride, an oil-gelling agent, in CO_2. The viscosity of the fluid phase increased several orders of magnitude using only 1wt% tributyltin fluoride, yet pentane co-solvent concentrations of 40-45 wt% were required, as shown in Figure5. Similar results, viscosity increases only in the presense of high concentrations of co-solvent, were obtained in the hydroxyaluminum disoap/co-solvent/CO_2system.



Viscosities of CO_2/Pentane/Tri-n-butyltin Fluoride Mixtures

Figure 5. Increase in Carbon Dioxide Viscosity for the CO_2/Pentane/Tributyltin Fluoride System

Although our attempts to identify a CO_2-thickener were unsuccessful, we did demonstrate that the perfluoroether functionality was highly CO_2-soluble. For example, the perfluorinated polyether (MW = 13,000) was CO_2-miscible in all proportions at room temperature at pressures above 18MPa (2600 psia). Similar experiments were conducted with a silicone oil of comparable molecular weight. The pressure required for complete miscibility in all proportions with CO_2 was 33 MPa (4800 psia). Although no significant viscosity increase was attained, we realized that the perfluoroether and siloxane functionalites were highly CO_2-philic. Therefore we are able to design and synthesize highly carbon dioxide-soluble compounds by replacing the alkylfunctional groups with fluoroether, siloxane, or fluoroalkyl moieties. For example, hydroxyaluminum di(2-ethyl hexanoate), an excellent propane thickener which forms helical micelles in solution, was found to be insoluble in carbon dioxide, leading us to synthesize hydroxy aluminum di(fluoroether carboxylate). Although this viscous liquid did not induce any significant change to the viscosity of carbon dioxide, it was **completely miscible** with CO_2 at a pressure of only 10 MPa at ambient temperature. The lack of any increase in viscosity was attributed to the formation of spherical, rather than cylindrical, micelles. Many other surfactants, dispersants and chelating agents have been synthesized in a similar manner for carbon dioxide-based reaction and separation applications. We also established that although these compounds were highly CO_2-soluble, they exhibited low solubility with light alkanes, such as pentane and octane, commonly used in ‘screening’ tests. *Thus it is imperative to test all thickeners in carbon dioxide, and not to rely on ‘screening’ in light alkanes.*

Recently, we developed fluorinated telechelic ionomers that require no cosolvent to dissolve in carbon dioxide. These compounds consisted of a fluoroether polyurethane, with molecular weight up to 30000, end-capped with sulfate groups. These disulfate molecules readily dissolved in carbon dioxide, as illustrated in Figure 6. The associations between the polar sulfate groups established a macromolecular network that resulted in an increase in carbon dioxide viscosity by a factor of three at a concentration of 4 wt% of the telechelic ionomer with a molecular weight of 30000, Figure 7.

Appendix A contains a summary of our current research in carbon dioxide viscosity enhancement.

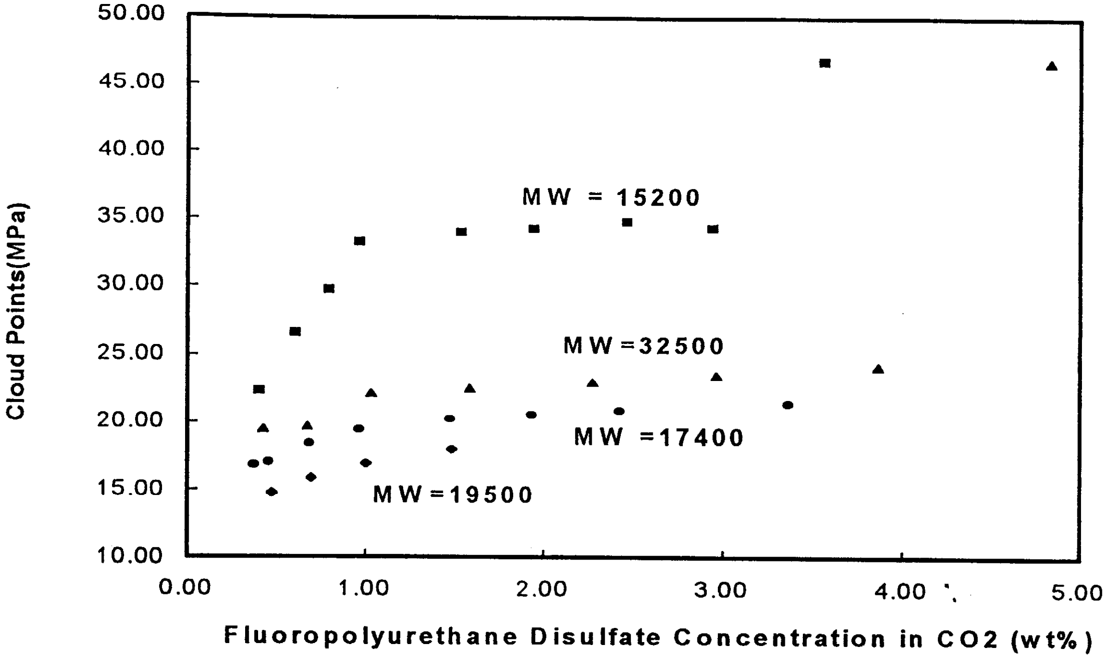


Figure 6. Solubility of Fluoroether-based Polyurethane Disulfates in Dense Carbon Dioxide at 298 K

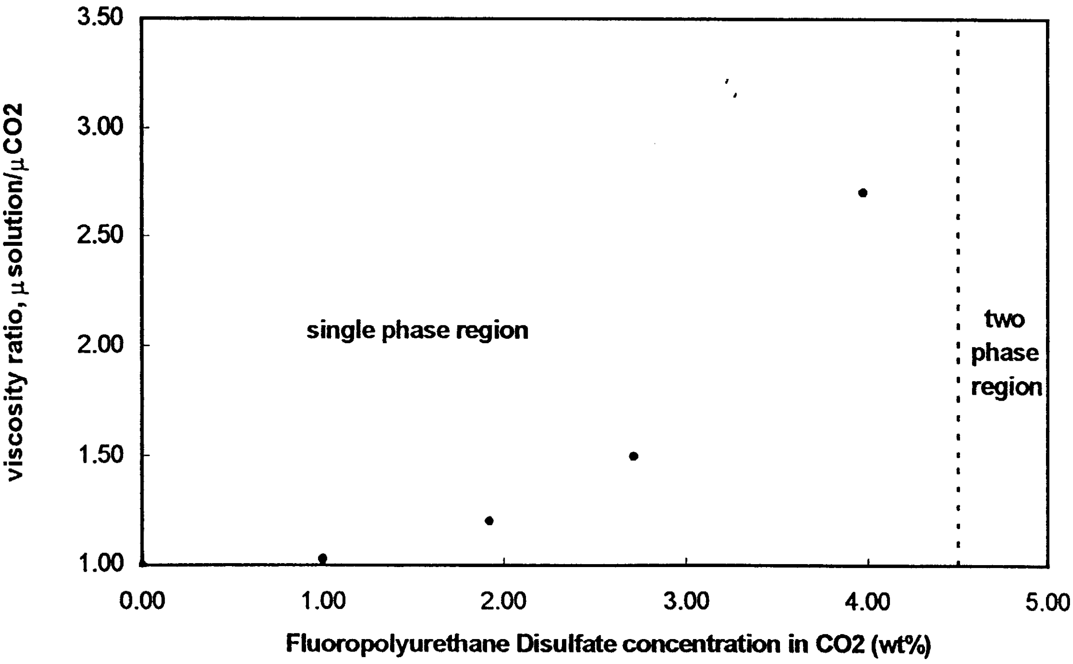


Figure 7. Viscosity of CO_2-Telechelic Ionomer Solutions Relative to Neat CO_2

University of North Carolina at Chapel Hill, DeSimone and coworkers, 1992-present

DeSimone and coworkers (37-41) have recently conducted numerous polymerizations in liquid and supercritical carbon dioxide. CO_2 has been shown to be a suitable reaction medium for homogeneous, precipitation, dispersion, and emulsion polymerizations. DeSimone has observed that fluoropolymers and silicones exhibit markedly greater solubility in carbon dioxide than other types of polymers. Viscosity changes associated with low concentrations of a highly CO_2-soluble homopolymer polymer in dense carbon dioxide have also been documented (37-38).

Poly(1,1-dihydroperfluorooctyl acrylate), PFOA, MW = $1.4*10^6$ g/mol, was formed by performing a homogeneous polymerization of the fluorinated monomer in carbon dioxide. This viscous, transparent liquid was able to induce a significant increase in solution viscosity as measured in a falling sinker viscometer. For example, at 50° C, the viscosity increased from 0.08 cp for neat CO_2 to 0.20- 0.25 cp at 280-360 bar using a 3.7 wt/vol% (3.7 gm polymer per 100 cm^3 solution) mixture of PFOA in carbon dioxide. At 6.7 wt/vol %, the viscosity increased from about 0.2 - 0.6 cp over the 230 - 350 bar pressure range. No co-solvent was required to dissolve this CO_2-philic polymer. Figure 8 is an illustration of the increase in carbon dioxide viscosity attained with PFOA at 50°C. *This is the only successful documentation of a polymer increasing the viscosity of carbon dioxide without the need for a co-solvent.* (We have recently confirmed these results with a perfluoropolyacrylate synthesized using Zonyl fluoromonomer manufactured by DuPont and sold through Aldrich. This polymer was formed in a fluorinated liquid at ambient temperature, and recovered by evaporating off the solvent. The polymer was then dissolved in liquid carbon dioxide at a 5 wt% concentration. A doubling of viscosity was detected at 298K and 5000 psia with a falling cylinder viscometer.)

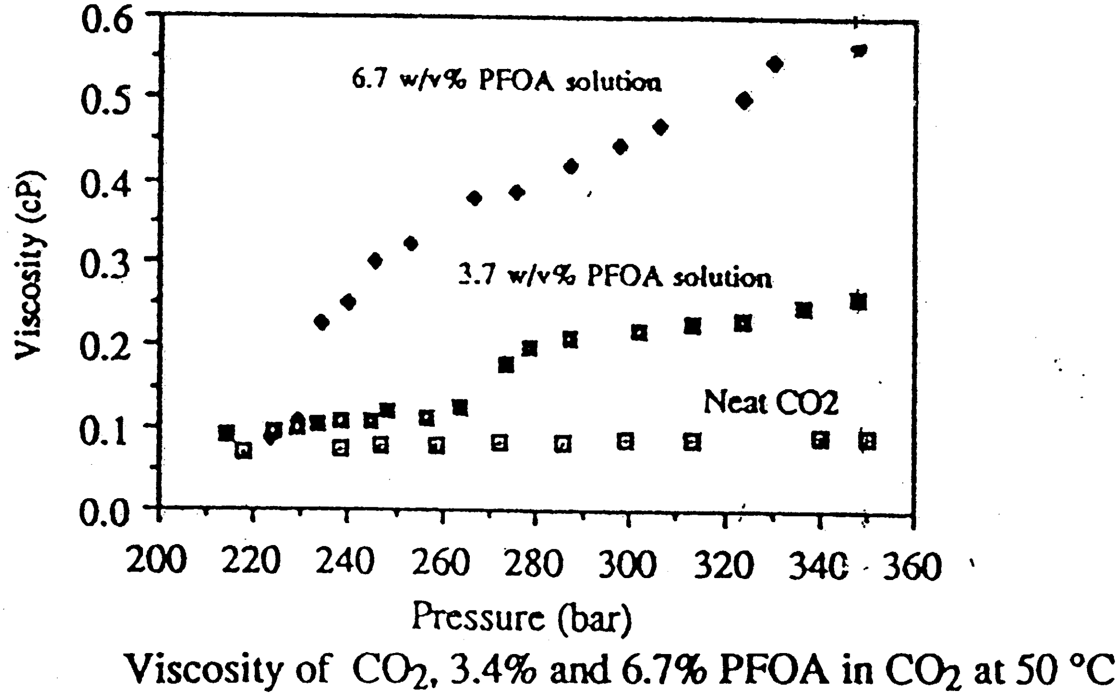
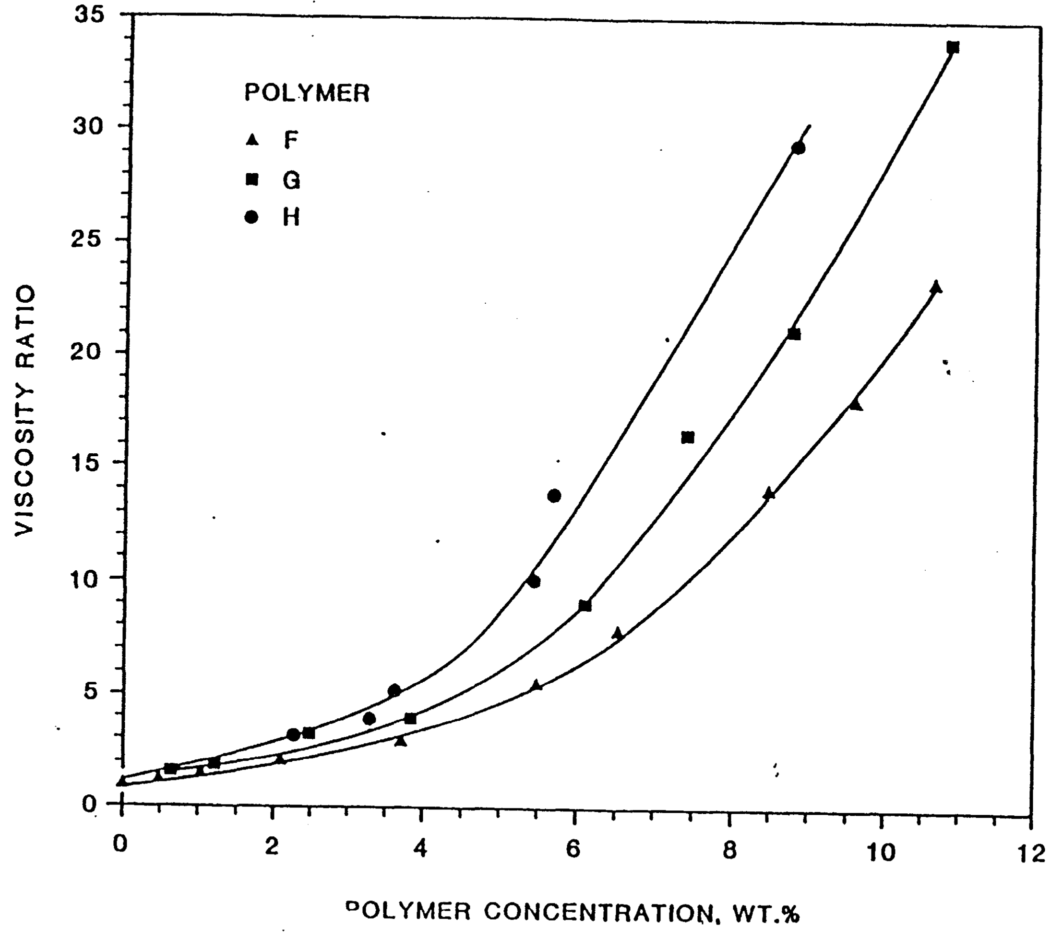


Figure 8. Increase in CO_2 Viscosity in the Carbon Dioxide/PFOA System, No Co-Solvent Required

Chevron - Davis, Harris, Irani, Pretzer, and Bae, 1989- present

Irani and Bae (42-43) reported that highly viscous CO_2 solutions could be attained with several weight percent of high molecular weight silicone oils. The polymers selected had a minimum solubility parameter of 6.85 or less and a sufficient amount of co-solvent was added to make the solution a single phase. A large amount of this co-solvent was required for the dissolution of the polymer, however. For example, they reported that 4wt% siloxane (MW = 197,000), 20wt% toluene, 76% CO_2 mixture at 130ºF and 2500 psia had a viscosity of about 1.5 cp. These researchers then clearly demonstrated that the use of viscous solutions of CO_2 in corefloods accelerated oil recovery and delayed CO_2 breakthrough in corefloods. Figure9 is an example of the increase in viscosity attained using admixtures of polymer and co-solvent.

Recently, Chevron was granted a series of patents (44-49) for polymer-co-solvent mixtures that were proposed for enhancing the viscosity of carbon dioxide. These polymers include polydialkylsilalkylenes, polymers containing pendant vinyl ether groups, polymers containing pendant tertiary alkyl amine groups, organosilicon polymers having non-random crosslinkages, polysilalkylenesilanes and polysilylenesiloxanes. Each patent includes guidelines for the selection of a co-solvent to enhance the carbon dioxide-solubility of the polymer.



PLOT OF CO_2 -POLYMER-TOLUENE VISCOSITY VS. POLYMER CONCENTRATION.
TOLUENE: 10 VOL.%. 3500 PSIG, 35°C.

Figure 9. Increase in CO_2 Viscosity for the CO_2/Toluene/Polydimethylsiloxane System, F = MW of 153000, G = MW of 193,000, G = MW of 197,000

1.4 Barriers to Development of a Carbon Dioxide Thickening Agent

The trends identified in the following section were therefore based on (a) the few successes in identifying carbon dioxide thickeners, (b) the results of systems containing significant amounts of co-solvent, and (c) the behavior of the thickening agents when use to increase the viscosity of oils.

Low Solubility in Carbon Dioxide, Leading to Large Amounts of Co-solvent or Expensive CO_2-Philic Compounds

The most significant barrier that continues to impede progress in the development of carbon dioxide-thickening agents is the low solubility of candidate compounds in dense CO_2. Although thickeners have been identified for light alkanes such as ethane and propane, all readily available carbon dioxide thickening agent candidates are sparingly soluble (on the order of 1/10th of a weight percent or less) in CO_2. Appreciable increases in viscosity can be observed only if large amounts of co-solvent, 10-20%, are introduced or if expensive, highly fluorinated carbon dioxide-philic molecules are designed. Thickener concentrations on the order of 1 to several weight percent are usually required for these compounds to induce a significant increase in viscosity.

Technical and Economic Barriers for Fluorinated Thickeners

Fluorinated acrylate polymers and fluorinated telechelic ionomers are the most promising thickening agent that have been identified for neat CO_2. Implementation in well-fracturing or EOR applications is hindered by several technical and economic barriers. The solubility of the polymer in CO_2 at low temperatures, the rate of dissolution of the polymer into CO_2 at low temperature and the solution viscosity at low temperatures must be determined. Although it is likely that this polymer will be an effective thickener at low temperature based on higher temperature results, a relatively large amount of the thickener (3-5 weight percent of the injected carbon dioxide) will be required. Upon depressurization, the polymer may damage the formation as it deposits as a solid or extremely visocus liquid in the formation and wellbore. This highly fluorinated deposit will be gas-, water- and oil-insoluble. Removal of the deposit can only be achieved with dense carbon dioxide or fluorinated liquids. Finally, fluorinated monomers and polymers are very expensive. For example, common fluorinated solvents cost about $10/lb, with fluorinated specialty chemicals costing over $100/lb.

Therefore 1 wt% of a fluoropolymer, such as the fluorinated polyacrylate or the telechelic ionomer, could be more expensive than the carbon dioxide used to fracture the formation.

Temperature

Significant decreases in polymer viscosity with increasing temperature will result in polymeric CO_2-thickener becoming less effective at elevated temperatures.   Some of the smaller molecules that self-assemble in solution to form pseudo-networks are not effective at moderate to high temperatures. Therefore a low MW carbon dioxide thickener may be developed that is effective at temperatures less than 30°C may be ineffective at temperatures at temperatures above 30°C.

Temperature will also affect the solubility of a thickening agent in dense carbon dioxide. In a constant density-, changing temperature-environment, the solubility of the thickener (a solid or highly viscous liquid) in carbon dioxide will probably be proportional to temperature.

Pressure

The foremost effect of pressure will be on the solubility of the thickening agent in carbon dioxide. If a carbon dioxide thickening agent can be identified, it is likely to exhibit solubility that is proportional to fluid density at a specified temperature. At a given temperature, carbon dioxide density initially increases with pressure (and goes through a liquid-vapor phase change if the temperature is less than the critical temperature of carbon dioxide) and then approaches a liquid-like density value. Therefore depressurization will lead to the deposition of the thickening agent (and co-solvent, if present) in a solid, viscous liquid, or solid-liquid phase mixture (depending on the identity of the thickener and co-solvent.) This deposition could lead to formation damage near the fracture.

Solubility of the Thickener in Natural Gas or Oil

The thickening agent that have been considered for carbon dioxide will exhibit much lower solubility in natural gas than carbon dioxide. Therefore any thickener deposited during the fracture of the formation, which may be in a solid, solid-liquid, or viscous liquid phase, will not be dissolved readily by natural gas as it flows toward the well. The thickening agent may be oil-soluble if it is a conventional oil-thickener used with a co-solvent. The thickening agent will be oil-insoluble if it contains fluorinated segments designed to increase carbon dioxide solubility.

Extremely Low Solubility of the Thickener in Water

Nearly all of the proposed thickening agents will demonstrate extremely low solubility in water or brine under reservoir conditions. Therefore these chemicals will not partition into an aqueous phase within the formation.

Emulsion Stability

Problems that are likely to be associated with the use of emulsions (as opposed to direct thickeners) to enhance the viscosity of liquid carbon dioxide include maintenance of the stability of the emulsion and the deposition of the oil-phase and surfactant within the formation upon depressurization of the carbon dioxide. Nearly all commercially available stabilizing agents, or surfactants, are designed for systems containing an aqueous phase and an oil phase. In this system, however, the phases are an oil-phase (the films) and a discontinuous liquid carbon dioxide phase (the interior of the bubbles). Many recent advances have been made in the design of surfactants for systems containing carbon dioxide by the DeSimone and Enick-Beckman groups. Although these surfactants will contain expensive silicone-based or fluorinated CO_2-philic segments that are carbon dioxide-philic, only small amounts of them may be need to stabilize the emulsion. The oil that is left within the formation will be slightly soluble in the natural gas and may eventually be ‘cleaned up’ during production.

1.5 Summary

A satisfactory CO_2 thickener has not yet been identified. The most common approach to identifying a viable thickener was to simply use compounds known to enhance the viscosity of oils because oils and liquid carbon dioxide are miscible or partially miscible. These hydrocarbon-based oil-thickening compounds have been ineffective carbon dioxide thickeners simply because dense CO_2 is a poor solvent, relative to oil, for these compounds and as such the thickeners were either insoluble or sparingly soluble in $CO_{2.}$. Conventional oil-thickeners (tributyltin fluoride, hydroxystearic acid, hydroxyaluminum disoaps, silicone oils) can be used only if a large amount of co-solvent (10-25 volume % of toluene, ethanol, etc.) is introduced.

The Enick-Beckman, DeSimone, and Chevron groups have determined that certain functionalities not commonly used in oil-thickeners, such as silicones, fluoroacrylates, fluoroalkanes, and fluoroethers, impart relatively high carbon dioxide-solubility. Polymeric thickening agents based on these CO_2-philic functionalities have exhibited significant solubility in $CO_{2,}$ reducing or eliminating the need for a co-solvent. Fluorinated acrylates with a MW of $1.4 * 10^6$ were also highly carbon dioxide soluble, and increased the viscosity of CO_2 from 0.08 cp to 0.6 cp, but only at concentrations of about 8 wt%. Telechelic ionomers with fluorinated polmers and polar head groups have also been shown to triple the viscosity of carbon dioxide at 4 wt%. These novel CO_2-philic compounds are very expensive, however, and near-term application is not likely, despite the absence of a need for co-solvent.

It appears that polymeric thickeners, whether the fluoroacrylates or silicone/co-solvent blends, are unable to induce a 10-fold (1000%) increase in carbon dioxide viscosity unless present in concentrations of 5-10 wt%. Although insoluble in neat CO_2, low MW associative thickeners, such as HSA, tributyltin fluoride, and hydroxyaluminum disoaps, form macromolecular structures in CO_2-co-solvent solutions that induce 10-100 fold increases in viscosity at concentrations of only 1-3wt%. Therefore, dilute concentrations of low MW compounds that associate or self-assemble appear to hold greater promise for 10-100 fold viscosity increases of carbon dioxide than high MW polymers. Although lower in molecular weight, these types of associative thickeners typically contain a polar group (e.g. alcohol, carboxylic acid, sulfonate) that enhances intramolecular interactions, but reduces CO_2-philicity.

Finally, the use of emulsions for this application should be reconsidered. Only the Canadian Fracmaster group has published extensively on this topic. These emulsions may contain an extremely high volume of liquid carbon dioxide and low volume and a small amount of an expensive surfactant. This appears to be the only technology that may be a viable option in the near-term due to the relatively low cost of the carbon dioxide and the non-aqueous phase (e.g. diesel fuel) and surfactant (even if the surfactant is expensive, only very dilute concentrations would be required). The stability of these emulsions has not been clearly substantiated in the literature, however. Although it has disadvantages (emulsion stability problems and deposition of the non-aqueous phase within the formation upon depressurization), recent advances in surfactant technology for carbon dioxide systems may lead to the development of more stable emulsions. Research groups at the University of Pittsburgh, the University of North Carolina at Chapel Hill and Carnegie-Mellon University are currently developing amphiphiles that can be tailored specifically to this application.

1.6 Guidelines for Design of Proposed Thickening Agents Based on the Literature Review

(1) *The thickener should not be tested in organic liquids during an initial screening.* Several of the most CO_2-soluble polymers and surfactants that we have identified exhibit low solubility in alkanes, which are commonly used in screening tests. Therefore these highly CO_2-soluble polymers would have failed in the screening test due to their poor solubility in light hydrocarbons!

(2) *Rather than testing hundreds of commercially available compounds, the thickener can be designed specifically for use in CO_2. This should increase CO_2-solubility while reducing or eliminating the need for a co-solvent.* We have pioneered the design and synthesis of a series of highly CO_2-soluble surfactants, chelating agents and dispersants for various reaction and separation processes by designing these amphiphilic compounds for CO_2-solubility (31, 50-62) without the need for co-solvents. This was achieved by incorporating CO_2-philic tails into the structure Figure 10. Functionalities such as fluoroethers and siloxanes have been used for the tails of these compounds, while conventional head groups have been selected for the appropriate application. We intend to apply this principle to the design of a CO_2-

thickening agent. Investigators conducting research in the chemical engineering applications of supercritical carbon dioxide have also confirmed the identity of these CO_2-philic functionalities (63-65). Unfortunately, these types of carbon dioxide-philic moities are very expensive.

(3) *If one desires to use commercially available thickening agents designed for oils, a co-solvent must be added.* Although this may provide the least expensive thickening agent in the near-term, significant amounts of organic liquids such as toluene or methanol are required to enable the thickener to dissolve in the carbon dioxide-rich solution.

(4) *Viscosity must be measured in the appropriate apparatus and flow range because of non-Newtonian nature of the thickened carbon dioxide solutions.* Although carbon dioxide could be considered a Newtonian fluid, the macromolecules used to thicken the solution will impart a non-Newtonian nature to the fluid. Whether polymers, small gelling compounds, or emulsions are employed, the thickened carbon dioxide will be non-Newtonian. Therefore the viscosity should be measured at shear conditions that exist at the wall of the fracture in an apparatus that is most appropriate for studying flow through slots.

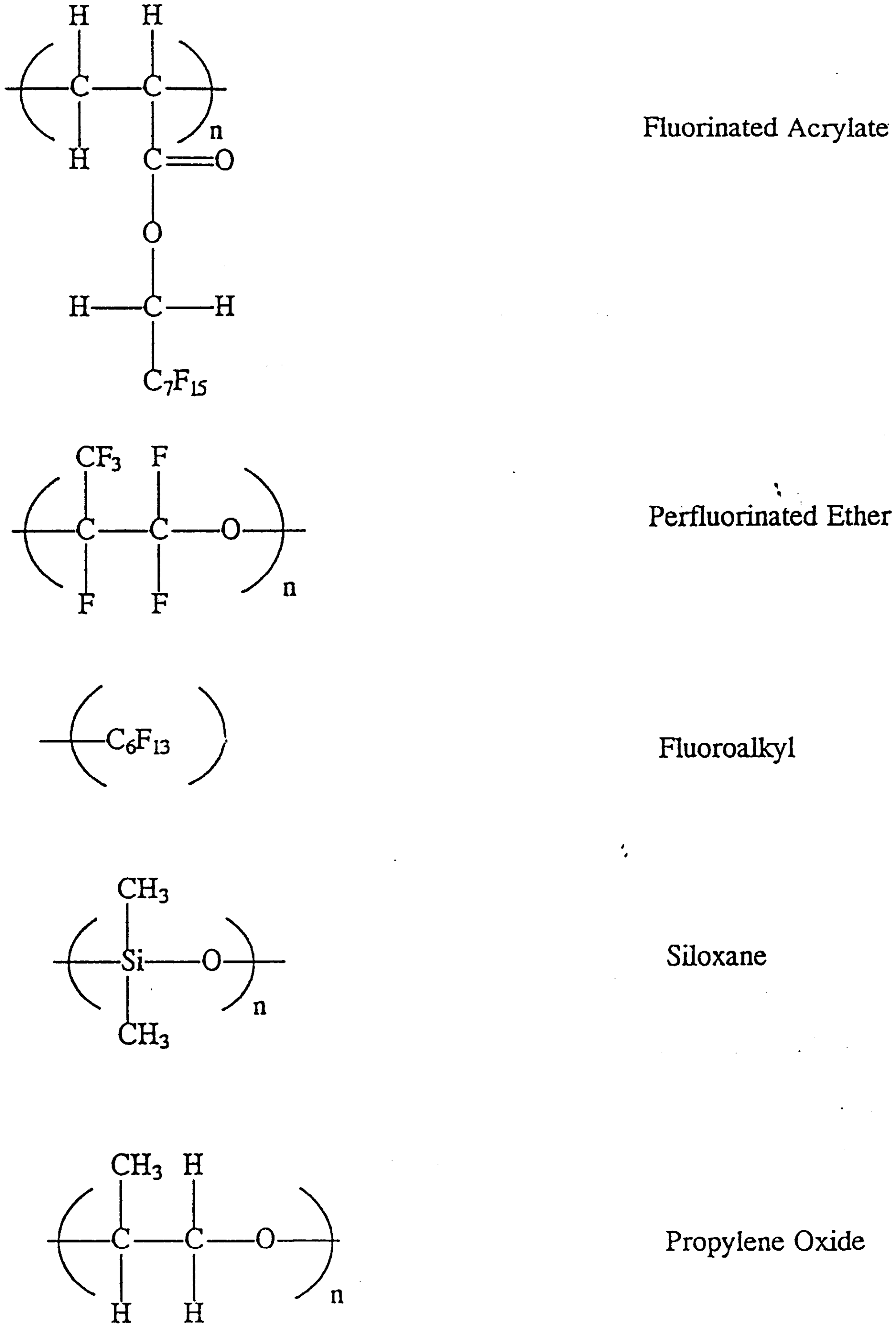
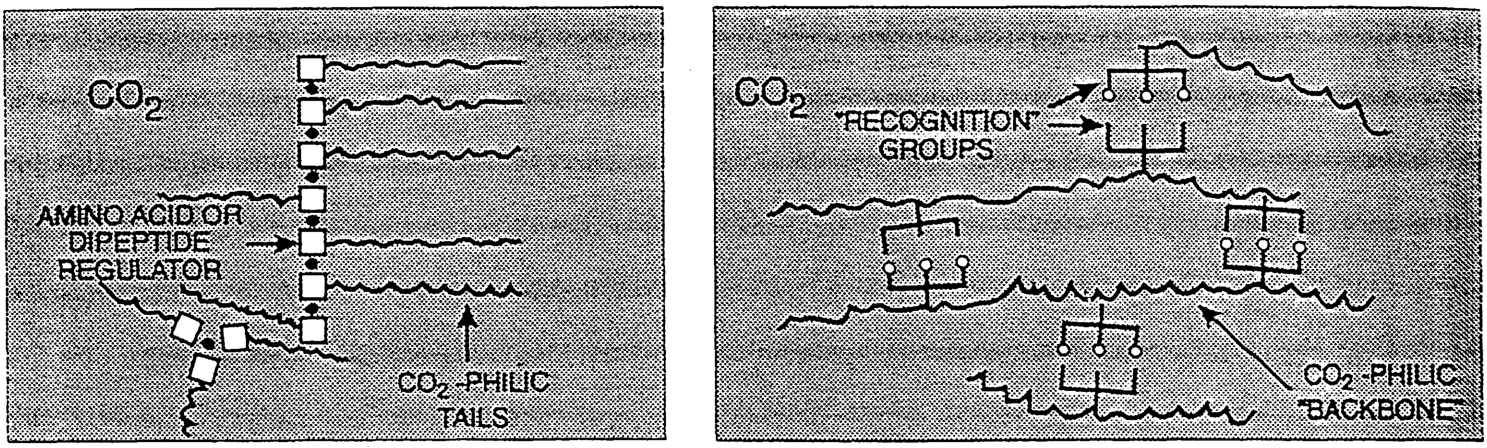


Figure 10. Carbon Dioxide-Philic Functional Groups

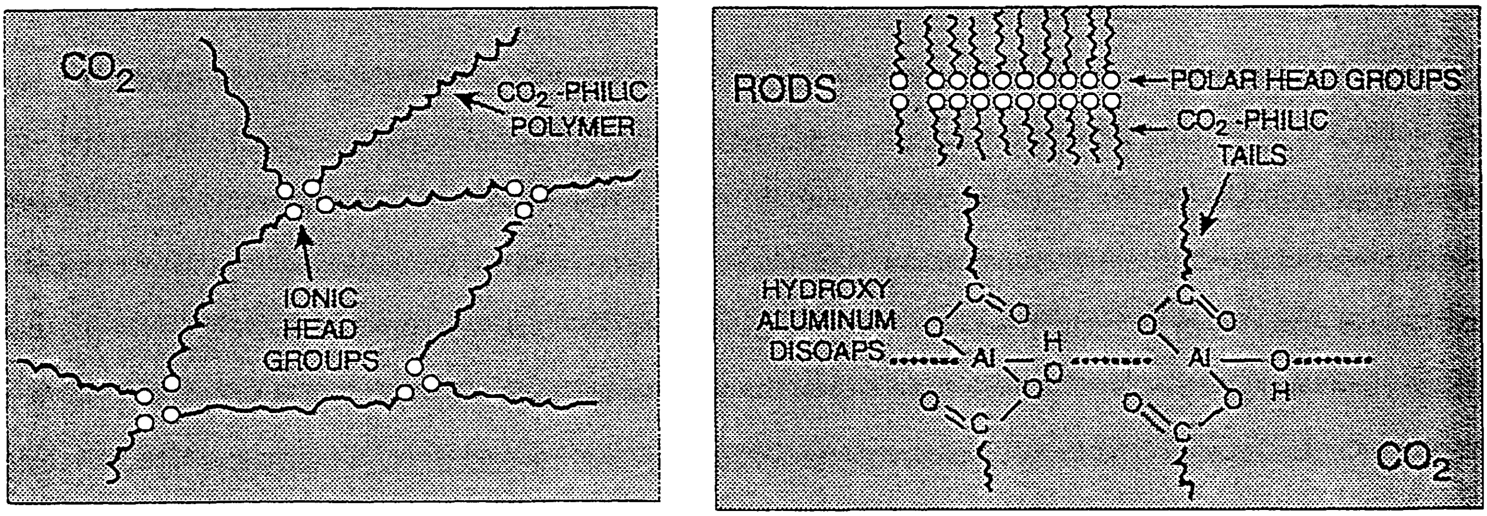
(5) *The thickener will work at lower concentrations if it is a relatively low molecular weight end-functionalized polymer or extremely low molecular weight compound that forms associative or H-bonded aggregates in solution, Figure 11, rather than an extremely high molecular weight polymer.* High molecular weight, random coil polymers designed for solubility in carbon dioxide will not increase the viscosity significantly unless present in unrealistically high concentrations, regardless of the repeat unit that constitutes a polymer. For example, the Chevron and DeSimone results indicate that at least 6wt% polymer is required for a 10-fold increase. The results of Heller and Enick indicated that increases of 1-3 orders of magnitude could be achieved with small gelling agents at concentrations of only 1-3% (although significant amounts of co-solvent were required). Lower molecular weight polymers or extremely low molecular weight gel-forming agents that contain polar functionalities that result in associations or self-assembly can induce the desired levels of viscosity increase when present in dilute concentration. These associating compounds form networks that, although not covalently bonded, have an incredibly high effective molecular weight, leading to viscosity increases of several orders of magnitude, Figure 11. Although ionomers and thickening agents that were known to gel oils have been previously considered as CO_2-thickeners (NMIMT, Univ. Of Pittsburgh), *we intend to continue synthesizing carbon dioxide-soluble versions of these types of molecules.*

(6) *Carbon dioxide emulsions can be designed using novel stabilizing agents*. The simplest emulsion system would contain liquid carbon dioxide, an anhydrous phase that is immiscible with the CO_2 at reservoir conditions, and a surfactant. The surfactant must be carefully designed because it contains two hydrophobic segments; a highly carbon dioxide-philic, oil-phobic segment and a highly oil-soluble, CO_2-phobic segment. Canadian Fracmaster has already reported several apparently successful field applications using a 98% carbon dioxide 2% anhydrous product referred to as 2P. 2P was a blend of a higher molecular weight fatty alcohol, a sorbitan fatty ester, and diesel oil. In the last 5 years, many new surfactants have been identified or developed by the DeSimone and Enick-Beckman groups that are effective in systems containing carbon dioxide. These new surfactants could lead to more effective, stable emulsions that require a single surfactant stabilizer, rather than a multicomponent blend.



HANABUSA-TYPE GELS

MOLECULAR RECOGNITION



ASSOCIATING POLYMERS

SURFACTANTS

Figure 11. Formation of Pseudo-Networks Using Small Gelling Agents Rather than High MW Polymers

(7) *An economic, short term solution to this problem is not currently available.* If one selects conventional thickening agents that are relatively inexpensive, a large volume of co-solvent will certainly be required. If one designs a novel thickener for carbon dioxide that will eliminate the need for a co-solvent, very expensive CO_2-philic functionalities (illustrated in Figure 10) must be used. If one chooses carbon dioxide emulsions with a second liquid phase (a low volume, non-aqueous phase that will constitute the films), difficulties may be encountered in selecting an appropriate stabilizing surfactant. In any of these cases, formation damage may occur upon depressurization.

APPENDIX A - Current CO_2-Thickening Research at the University of Pittsburgh

Viscosity-Enhancement Mechanisms - Effect of Molecular Weight

Flory's original derivation for the effect of random-coil macromolecule properties on the viscosity of solutions shows that the relative viscosity (the ratio of solution to solvent viscosity) in the dilute regime is proportional to $(1 + [\eta]c)$, where $[\eta]$ is the intrinsic viscosity (in effect, the contribution to solution viscosity from individual polymer molecules). In addition, the intrinsic viscosity is known to vary with molecular weight (again, for random coil polymers) via the following relationship:

$$[\eta] = KM^{a} \qquad 1$$

where M is the molecular weight and K and a are material parameters (Mark-Houwinck parameters). In dilute solutions, a has been found to vary between 0.5 (poor solvents) and 0.8 for flexible chains. For a typical polymer (100,000+ molecular weight, random coil) in a good solvent (polystyrene in toluene, in this example), the intrinsic viscosity is approximately 0.1 m^3/kg at room temperature. Consequently, to generate a relative viscosity of 10 or more (an order of magnitude increase in viscosity), we would require a concentration of approximately 8 to 10 weight percent. This order-of-magnitude estimate is in general agreement with the previously described results of DeSimone and coworkers at University of North Carolina at Chapel Hill for extremely high molecular weight fluorinated polyacrylates and that by Irani, Davis and coworkers at Chevron for high molecular weight silicone-based polymers. This concentration is well beyond what could be considered for use in CO_2-flooding. As such, we must abandon the use of conventional flexible coil polymers as a realistic approach to the problem if dilute concentrations of the thickening agent are desired.

Given this background, we will propose methods by which one can increase the viscosity of carbon dioxide by greater than an order of magnitude. Each of these relies on the formation of very large molecular structures in carbon dioxide using relatively low molecular weight compounds that associate or self-assemble in solution. This will allow us to effectively enter the concentrated regime of viscosity-composition behavior, and ultimately to form a three-dimensional network, while employing relatively small amounts of solute.

Formation of Non-Covalent Networks in Carbon Dioxide

Equation 1 is valid for the viscosity of dilute polymer solutions, that is, concentrations below the point at which the polymer coils do not overlap in solution. The viscosity of concentrated solutions (ie., concentrations above the overlap point) varies as $M^{3.4}$, which is thought to be due to the presence of interchain entanglements acting as temporary crosslink points. The approach to gel formation, which results in an infinite molecular weight (and thus infinite viscosity), provides a viscosity relationship shown in equation 2:

$$\eta = \eta_0 (p_c - p/p_c)^{-k} \qquad 2$$

where η_0 is the viscosity of the solvent, p is the fraction of possible crosslinks which have actually formed, and p_c is the fraction of crosslinks which results in gelation. Clearly, it would be desirable to operate either in the concentrated regime or to approach gelation, where formation of crosslink points leads to rapid viscosity build-up. However, we do not wish to employ large weight fractions of solute or to generate a viscosity which is so high as to completely prohibit flow. *Consequently, we propose to generate non-covalent crosslink points in a dilute solution through the incorporation of functional groups in our solute molecules which interact strongly in solution.* A conventional example of this strategy is the use of ionic cations as crosslinking agents for carboxylic acid-functional polymers in aqueous solution. In our case, we shall make use of the extensive recent literature on the application of hydrogen-bonding moieties to form extensive networks (gels) in solution. In addition, we shall draw upon our experience in the generation of highly CO_2-soluble macromolecules through the use of "CO_2-philic" functional groups, ie., moieties which exhibit more favorable thermodynamic interactions with carbon dioxide than conventional alkyl groups.

Although "gel" is a somewhat nebulous term, for the purposes of this work we can describe a gel as a reversible network formed through generation of non-covalent crosslink points in a single phase, homogeneous, CO_2-rich solution. We can further divide this definition into gels formed via crystallization and gels formed through hydrogen bonding, acid-base or ionic interactions. We will consider only the latter group, and will neglect gels formed through generation of crystallite crosslinks. We must therefore consider incorporation of strongly associating functional groups to form crosslink points. Our goal is to increase the viscosity of the dense carbon dioxide by only 1-2 orders of magnitude, as opposed to the 4-6 order of magnitude increase associated with gels, where smaller concentrations of gelling agents or less efficient gelling agents can be used to achieve the desired increase in viscosity.

CO_2-Philic Functional Groups

Many investigators, especially in the last decade, have attempted to determine the characteristics of carbon dioxide-philic compounds. For example, fluids are generally thought to have a high probability of being miscible if their solubility parameters are comparable. Calculations of the solubility parameter for carbon dioxide would suggest that CO_2 exhibits solvent power at high pressure which resembles that of liquid alkanes. Many investigations, especially those of Heller and coworkers, have shown that this measure alone is not a sufficient indication of the carbon dioxide solubility of a compound, as evidenced by the carbon dioxide insolubility of many light alkane soluble polymer and associative thickeners. However, Johnston has shown that the quadropole moment of CO_2 inflates the calculated solubility parameter by approximately 20%, which suggests that CO_2 is more like a fluorinated alkane or a silicone than a liquid alkane, where solvent power is concerned. Fluoroethers, for example, have the lowest solubility parameter of any conventional liquid and exhibit extremely high carbon dioxide solubility. Further, carbon dioxide is a Lewis acid, and thus one might expect that CO_2 would exhibit specific interactions with Lewis bases, which are quite unlike liquid alkanes. Further, fluorinated alkanes and liquid carbon dioxide are the only types of compounds that exhibit negative dipolarity/polarizability parameters, π^* (66-71). The π^* scale of solvent strength is a solvatochromic measure of polarizability and dipolarity. Similarity of these parameters provides an indication of enhanced miscibility. *Ab initio* electronic structure calculations by Cece (72) suggest that specific interactions between individual fluorines and carbon dioxide contribute to favorable mixing behavior. Eckert's work suggests that the effect of fluorinated groups on the electronic character on the neighboring carbonyl group contributes to stronger interactions between that group and carbon dioxide. The experimental results of Yee and coworkers (73) led them to speculate that repulsion between fluorinated compounds was responsible for their increased solubility in carbon dioxide.

In our previous research, we have explored the generation of amphiphilic compounds (polar head group and hydrophobic tail; ie., surfactants and chelating agents) *where the conventional alkyl tail is replaced with either fluoroalkyl, fluoroether, siloxane or propylene oxide functional groups*. We have found that substitution of these CO_2-philic groups for -CH_2- will increase the solubility of the target molecules by several orders of magnitude in carbon dioxide (31,50-62). In addition, we have observed inverse emulsion formation in carbon dioxide/water mixtures when these CO_2-philic surfactants are employed. However, not all fluorinated compounds behave similarly in mixtures with carbon dioxide. Chilluramartino (74) has used second virial coefficient calculations based on neutron scattering results to show that carbon dioxide is a better solvent for fluorinated acrylates than for fluoroethers. In fact, it is apparent that the entire class of fluorinated compounds does not exhibit high solubility in carbon dioxide. For example, although Teflon swells slightly in the presence of liquid or supercritical carbon dioxide, it is commonly used as a seal for high pressure vessels that contain dense CO_2. Although DeSimone and colleagues (37, 38, 75) have dissolved fluoroacrlyate polymers in carbon dioxide at moderate pressures, McHugh and coworkers (63) reported that fluorinated ethylene-propylene copolymers require order-of-magnitude higher pressures to achieve comparable solubilization. It is interesting to note that the most carbon dioxide soluble polymers, the fluoroacrylates and the fluoroethers, are fluorinated, contain ether linkages, and are transparent viscous liquids at ambient conditions. Fluorinated polymers that are solid at ambient conditions (ie. Have high T_g or T_m) are typically more carbon dioxide-soluble than their hydrocarbon analogs, but are less carbon dioxide soluble than the fluorinated acrylates or ether polymers. Finally, although these carbon dioxide-philic functional groups are more CO_2 soluble than their alkyl-analogs, they become less miscible with carbon dioxide as their MW increases.

Although the exact mechanisms responsible for the enhanced solubility of fluorinated and silicone based compounds in carbon dioxide have not been positively identified, it is apparent from the results of numerous investigators, including our extensive work in this area, that highly CO_2-soluble functional groups exist and can be used to enhance *the CO_2-solubility of polymers, surfactants, dispersants, and chelating agents. It is our intent to extend this list of applications to include carbon dioxide thickening agents.* Consequently, our model viscosity-enhancing solutes will contain these CO_2-philic groups, namely fluoroalkyl, fluoroether, fluoroacrylate, siloxane, and propylene oxide, Figure 10, in place of the -CH_2- units in the nonpolar regions of the associative thickeners developed in this study. The thickeners will consist of very small gelling agents that can H-bond or associate in solution, or relatively low ME end-functionalized polymers that can form viscosity enhancing pseudo-networks in solution. Examples of how small gelling agents form pseudo-networks are presented in Figure 11.

Statement of Current Research for Proposed Generation of Viscosity-Enhancing Agents at Univ. Of Pitt

Two types of viscosity-enhancing agents will be considered in this study. Each type of thickener has been previously demonstrated to be in gelling oils. In oil-thickening applications, these thickening agents typically contain an alkyl- non-polar group to enhance oil-solubility and a polar group to facilitate the interactions required to establish a macromolecular structure. *We intend to synthesize carbon dioxide soluble-analogs of each using carbon dioxide-philic functional groups in place of the alkyl groups, measure the solubility in dense carbon dioxide, and determine the viscosity of these dilute solutions.* As observed in these previous studies, we expect to find an optimum MW of the CO_2-philic portion for these gelling agents. If the CO_2-philic portion is too small, the agent will be too polar to be soluble in carbon dioxide. As the MW of the CO_2-philic portion increases, the influence of the polar head group on CO_2-solubility will be reduced and the gelling agent will become more carbon dioxide-soluble. If the MW of the CO_2-philic portion becomes too great, however, the carbon dioxide solubility will again decrease simply because the MW of the agent is too high. *Therefore, carbon dioxide solubility of amphiphilic compounds with a specified polar group(s) increases, reaches a maximum value, and then decreases as MW of the carbon dioxide-philic portion of the gelling agent increases.* We intend to design the gelling agent such that the CO_2-solubility is on the order of one weight percent, the concentration typically needed to induce significant changes in fluid viscosity.

Formation of Gels in Carbon Dioxide

There are a number of reports in the literature where molecules have been shown to form large structures in solution, thus effectively gelling the organic solvent in which they have been dissolved. We have selected two classes of carbon dioxide thickening agents for this work, (a) relatively low molecular weight, end-functionalized polymers referred to as ionomers and (b) small gel-forming compounds. *These ionomers and gel-formers will be designed to exhibit carbon dioxide-solubility by incorporating CO_2-philic functional groups into the non-polar regions of the molecules that are designed to be miscible with dense carbon dioxide. Conventional polar groups will be selected for the intermolecular interactions required to establish a macromolecular network.*

Although it is not necessary to 'gel' the carbon dioxide, *gel-forming compounds are typically able to induce the desired 10-100 fold increase in viscosity if they are used at lower concentrations*.

Recent work by Hanabusa et al., Hamilton and coworkers at the University of Pittsburgh, and others (76-105) has shown that small amphiphilic materials will form gels in a wide variety of organic solvents at low concentrations (2 to 20 grams/liter). We propose to generate the CO_2-soluble version of several of these materials, where the alkyl functional groups will be replaced by (a) fluoroether, fluoroacrlyate, or fluoroalkyl, (b) silicone, and (c) propylene oxide groups. We propose to evaluate several types of CO_2-philic groups because while fluoroethers will likely provide for higher solubility at lower pressure, the propylene oxide-based material will be significantly less expensive to produce, and is likely to be biodegradable as well. In work on generation of polyurethanes in carbon dioxide, we have found that typical propylene oxide polyols exhibit significant solubility in carbon dioxide at moderate pressures although less than that of the fluoroether or fluoroalkyls. Given the other benefits of propylene oxide based materials (cost, biodegradability), we feel that it is worthwhile to investigate PO-functional gelling agents. Indeed, an optimized material may contain several types of groups, in order to maximize solubility while minimizing cost.

Telechelic Ionomers

Although our strategy precludes the use of carbon dioxide soluble ultrahigh molecular weight polymers, we will attempt to form macromolecular structures using carbon dioxide soluble, low molecular weight polymers that form viscosity-enhancing networks in solution. It has been shown that one can end-functionalize polymers with ionic groups such that the ionic moieties form associates in solution (106-109). Polar head groups that have been shown to induce these molecular associations include sulfates, sulfonates, and carboxylic acids. The relative viscosity (ratio of solution to solvent viscosity) of solutions of these materials in organic solvent approached 10^6 at concentrations of less than 5 weight percent. 10-100 fold increases in viscosity have been accomplished at concentrations of approximately 1-2 wt%. Heller also considered this type of thickener in his research at NMIMT in his evaluation of sulfonated polyisobutylene. Although hydrocarbon-based solvents can be caused to gel, it is almost certain that the polymers described in these examples would exhibit vanishingly small solubilities in carbon dioxide at the temperatures and pressures which are commonly encountered in typical reservoirs. Hydrocarbon-based polymers are essentially insoluble in carbon dioxide and the addition of polar end groups to these compounds will further reduce CO_2-solubility. *Our efforts, however, will be directed at designing carbon dioxide-philic ionomers using carbon dioxide-soluble polymers such as fluoroethers and fluoroacrylates which are likely to exhibit appreciable carbon dioxide solubility, even when functionalized*. We have already successfully designed CO_2-soluble surfactants and chelating agents that contain polar groups using this strategy (31, 35, 36,50-61). Consequently, we propose to synthesize and evaluate the CO2-soluble associating polymers in order to produce gels in CO_2. *We have recently developed our first carbon dioxide-thickening telechelic ionomer, a fluorinated polyurethane disulfate, capable of tripling the viscosity of carbon dioxide at a4wt% concentration.*

Significance of Expected Results

Nearly all previous attempts to identify a carbon dioxide thickening agent have been frustrated by the insolubility of viscosity enhancing agents in dense carbon dioxide. The few cases in which a substantial increase has been reported required large amounts of a hydrocarbon co-solvent. Rather than continuing to evaluate every compound known to thicken oil in hopes that it will dissolve in CO_2, we have presented a strategy for designing thickeners that will exhibit high carbon dioxide-solubility. *We have already accomplished this goal in the design of amphiphilic compounds that* *are typically insoluble in* CO_2*, such as surfactants dispersants and chelating agents. We have recently identified one telechelic ionomer that has displayed thickening potential.* We will incorporate CO_2-philic functionalities, such as fluoroethers, fluoroacrylates, fluoroalkyls and siloxanes, into these compounds to enhance carbon dioxide miscibility. Polar groups known to cause intermolecular associations that lead to the formation of viscosity-increasing macromolecules. The most challenging portion of the proposed work will be to design the gelling agent such that the balances the contributions of the polar group (which diminishes CO_2-solubility but is required for H-bonding or associations leading to pseudo-network formation and viscosity increases) and the carbon dioxide-philic segment (which must be long enough to make the gelling agent CO_2-soluble but can lead to carbon dioxide solubility if it is too high in MW). The solubility and viscosity of the solutions will be determined using standard techniques. *If successful, this work will result in the first class of compounds capable of increasing the viscosity of carbon dioxide when present in dilute concentration and without the need for co-solvents.*

We are also capable of developing surfactants that can stabilize low temperature emulsions that have been considered for well-fracturing applications. Unlike commercially available surfactants, these molecules can be designed to have a carbon dioxide-philic portion and a segment that is soluble in the non-aqueous phase, whether it is diesel fuel or a water-alcohol blend. *This technology could possibly be used in the short-term for stabilizing carbon dioxide emulsions because of the verysmall amounts of surfactant typically needed to stabilize an emulsion.*

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