NOVEL CO₂-THICKENERS FOR IMPROVED MOBILITY CONTROL

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Abstract

A detailed study of the viscosity of carbon dioxide-poly(fluoroacrylate-styrene) copolymers was conducted. Falling cylinder viscometry experiments were conducted over a wide range of shear rates and polymer concentrations. The tests were conducted at ambient 297 K and 34 MPa. Results demonstrated that the solution viscosity increased with polymer concentration. The solutions also exhibited shear thinning behavior, with increasing viscosity observed at lower shear rates. This viscometer could not yield data at relatively low viscosity increases (2-10 fold increase) and low shear rates ($10\text{-}20\text{s}^{-1}$) desired for EOR applications. Extrapolations of dilute solution results, however, indicated that it may be possible to increase the viscosity of dense carbon dioxide by a factor of 2-3 at low shear rates using very dilute polymer concentrations.

Executive Summary

The objective of this contract is to design, synthesize, and characterize thickening agents for dense carbon dioxide and to evaluate their solubility and viscosity-enhancing potential in CO₂. Hydrocarbon-fluorocarbon random copolymers, sulfonated hydrocarbon-fluorocarbon random copolymers, semifluorinated trialkyltin fluorides and small hydrogen-bonding compounds have been evaluated. Random copolymers of styrene and heptadecafluorodecyl acrylate yielded substantial increases in viscosity. Falling cylinder viscometry results indicated that the 29%styrene-71%fluoroacrylate bulk-polymerized copolymer induced very significant viscosity increases at copolymer concentrations of 0.1-5.0wt%.

A detailed study of the poly(fluoroacrylate-styrene) carbon dioxide thickener was completed this quarter. Close-clearance falling cylinder viscometry was used to measure solution viscosity. Aluminum cylinders of varying diameter (and therefore terminal velocity and shear rate) were used to determine the effect of shear rate on viscosity. Further, concentrations as low as 0.1wt% were tested in an attempt to identify the lowest concentration of thickener required to enhance the viscosity of dense carbon dioxide. The results indicated that the solutions were shear-thinning, and that viscosity increased with increasing concentration. The increase in viscosity attained using dilute concentrations of the thickener could not be determined with this apparatus at low shear rates (in the range of EOR floods). Extrapolated results from higher shear rates indicated that it *may* be possible to achieve 2-fold increases in carbon dioxide viscosity using polymer concentrations of 0.1-0.2 wt%.

These falling cylinder viscometry results serve as a screening tool for identifying compounds that completely dissolve in carbon dioxide and can significantly increase the solution viscosity. More accurate and relevant viscosity measurements will be generated in the second year of the project for promising carbon dioxide-thickeners by measuring pressure drops associated with a specified flow rate of the solution through sandstone cores.

1. Introduction

Carbon dioxide is non-flammable, relatively non-toxic, and naturally abundant, and is consequently promoted as a sustainable solvent in chemical processing. Carbon dioxide's "green" properties have provided the driving force for development of a number of new applications, such as replacement of organic solvents in polymerization [1-3], as a medium for conducting hydrogenations and oxidations in the absence of transport limitations [4, 5], as a solvent in biocatalysis [6], and as a raw material in synthesis [7,8]. Many of these applications have been made possible by the relatively recent discovery that certain functional groups, subsequently christened "CO₂-philic", enable miscibility of target compounds with CO₂ at moderate pressures [9]. Development of CO₂-soluble surfactants, for example, has rendered CO₂-based emulsion polymerization and dry cleaning feasible. Design and synthesis of CO₂-philic phosphine ligands has spawned a number of CO₂-soluble metal catalysts. In this paper we show how combination of concepts in CO₂-philic design with an understanding of molecular assembly in solution has allowed us to gel CO₂. Creation of gels in carbon dioxide allows us to attack two problems that have frustrated engineers for decades: (a) how to raise the viscosity of CO₂ to permit more efficient enhanced oil recovery, and (b) how to generate cellular polymers with a bulk density less than 10% of the parent polymer and cells smaller than 10 microns. Generation of gels in CO₂ provides solutions to these problems that are both technically and environmentally satisfying.

The pressure gradient between oil-bearing porous media and a production well is initially the force that moves oil to the wellhead. As the formation pressure drops during production, a flooding agent (usually water) is pumped into the oil-bearing formation to maintain the reservoir pressure and to displace additional petroleum to production wells [10]. Although the water sweeps efficiently through the formation, it displaces only a small fraction of the oil it encounters because water and oil are effectively immiscible. Dense carbon dioxide is miscible with petroleum, and thus will displace (tertiary recovery) the oil left behind by water-flooding. However, the viscosity of CO₂ can be 100 times lower than the viscosity of the oil, and thus carbon dioxide "fingers" its way through the petroleum rather than sweep the oil before it. The displacement efficiency is very high where the CO₂ actually contacts the oil, but by fingering the CO₂ bypasses most of the petroleum in the formation. Petroleum engineers have tried for decades to design an additive [11] that can raise the viscosity of carbon dioxide (at low

concentration) to a level comparable to the oil being displaced, thereby inhibiting the formation of “fingers”. Success, unfortunately, has been elusive. Additives have been synthesized that enhanced the viscosity of simple *hydrocarbons*, yet which were not soluble in CO₂ without the use of impractically high fractions of co-solvent [12,13]. On the other hand, surfactants have been designed that are CO₂-soluble, but their effect on the viscosity has been minimal.

In this report, we show how one can design molecules that are both highly CO₂-soluble and which aggregate in solution. When associating polymers are employed, we have observed the 2 order of magnitude increase in viscosity, as determined by falling cylinder viscometry. The shear rate- and concentration-dependence of the solution viscosity are reported.

2. Experimental Procedure

Polymer Synthesis

Heptadecafluorodecylacrylate-Styrene Copolymer

Bulk polymerized 79%heptadecafluorodecyl acrylate - 21% styrene random copolymers are the most promising carbon dioxide thickeners identified to date. They can increase the viscosity of carbon dioxide by a factor of 250 at a concentration of 5wt%. We postulate that

- a. bulk polymerization leads to higher copolymer molecular weight
- b. the fluoroacrylate monomer enables the copolymer to dissolve in carbon dioxide
- c. the styrene monomer leads to macromolecular formation via pi-pi stacking, but also causes the copolymer to become less carbon dioxide-soluble
- d. increasing the fraction of styrene in the copolymer from 0-29% results in the *intermolecular* “stacking” of aromatic rings (associated with the styrene monomer), leading to viscosity-enhancing macromolecular formation in CO₂ solutions
- e. increasing the fraction of styrene beyond 29% leads to the polymer coiling upon itself (because it is becoming more carbon dioxide-phobic) and *less effective* viscosity-enhancing *intramolecular* associations of the aromatic groups

Because the heptadecafluorodecyl acrylate monomer is very expensive and not available in bulk volume, several commercial grade fluorinated acrylate monomers were considered.

Perfluoroalkylethacrylate-Styrene Copolymers

Asahi Glass FA-X monomer is a relatively inexpensive commercially available polydisperse perfluoroalkyl ethyl acrylate monomer. The carbon chain length of the fluorinated tail is 6-16, 2-perfluoroalkyl(C6-C16)ethyl acrylate. Because the structure of the perfluoroalkyl ethyl acrylate monomer is similar to the heptadecafluorodecyl acrylate, we examined the possibility of generating FA-X – styrene copolymers for CO₂-thickening. The synthesis of FA-x homopolymer is similar to the synthesis of copolymer. FA-X alone was employed as the monomer, however.

We synthesized both the homopolymer of FA-X and random copolymers of FA-X and styrene. The following steps were employed during the synthesis of the random copolymers.

1. Purify the FA-X: Wash FA-X with 5% NaOH three times, wash it with distilled water three times, add MgSO_4 to remove trace water, put it into refrigerator, filter it to get purified FA-X.
2. Use AIBN as initiator, put 0.2% (mol) of AIBN into ample.
3. Add specific amount of distilled styrene.
4. Add specific amount of purified FA-x into ample.
5. Send N_2 into ample to remove O_2 , seal the ample.
6. Put the ample in silicon oil (60°C), overnight.
7. Use Freon 113 to dissolve the copolymer, and wash the copolymer with methyl alcohol several times.

The carbon dioxide solubility results of the perfluoroalkyl ethyl acrylate – styrene copolymers and the perfluoroalkyl ethyl acrylate homopolymer were not promising. We were unable to dissolve either in dense carbon dioxide. *Therefore we will not use fluoroalkyl ethyl acrylate (or fluoroalkyl methyl acrylate) monomers in any future thickening agents.* The presence of the small alkyl group (methyl or ethyl) on the fluoroalkyl acrylate monomer leads to substantial decreases in carbon dioxide solubility of polymers.

Fluoroalkyl Acrylate-Styrene Copolymers

3M and Elf Atochem produce commercial amounts of a fluoroalkyl acrylate for the manufacture of fluoroacrylate copolymers. We have contacted both companies and are attempting to obtain samples of their fluoroalkyl acrylate monomers.

Falling Cylinder Viscometry

Based on our previous findings, the 29%styrene-71%fluoroacrylate copolymer showed the greatest promise. Therefore we conducted a thorough falling cylinder viscometry assessment of its carbon dioxide thickening potential. The copolymer was CO_2 soluble, and the mixture of copolymer and CO_2 was transparent. We have previously presented the details of the solubility of the polymer in carbon dioxide.

Falling cylinder viscometry [14-16] was conducted by observing the terminal velocity of an aluminum cylinder falling through neat carbon dioxide or a single phase, transparent solution of carbon dioxide and the copolymer. The ratio of the terminal velocities (velocity in neat carbon dioxide/velocity in thickened carbon dioxide) was directly proportional to the increase in viscosity. Each terminal velocity experiment was repeated 5-7 times.

The major characteristics of the high pressure falling cylinder viscometer are summarized in the following table.

Cylinder material	Aluminum
Cylinder specific gravity	2.7
Cylinder length	0.8268 in
Cylinder #1 diameter	1.2450 in
Cylinder #2 diameter	1.2438 in
Cylinder #3 diameter	1.2428 in
Cylinder #4 diameter	1.2399 in
Cylinder #5 diameter	1.2339 in
Cylinder #6 diameter	1.2311 in
Cylinder #7 diameter	1.2293 in
Cylinder #8 diameter	1.2269 in
Quartz hollow cylinder ID	1.2500 in
Distance travelled by falling cylinder	5-12 cm
Fluid	Neat CO ₂ or thickened CO ₂

Table 1. Characteristics of the Falling Cylinder Viscometer

3. Viscometer Calibration Constants and Example Calculations

Theoretical and experimental calibration constants

From derivation, we assume the CO₂ solution is Newtonian fluid, so,

$$\mu = K \frac{\rho_c - \rho_f}{V_c}$$

Then, we can compare the experimental calibration constant K with the theoretical calibration constant, ignoring the resistances because non-ideal falling.

In our falling cylinder viscometer, we use pure CO₂ as our sample, at specific temperature (297K), and specific pressure (3000psi), we can get experimental calibration constant:

$$K = \frac{\mu V_c}{\rho_c - \rho_f}$$

We can also get theoretical calibration constant from the size of the falling cylinder:

$$K = \frac{r_c g}{r_c J' - 2K'}$$

Where,

$$J' = -\frac{4}{(r_i^2 - r_c^2) + \ln \frac{r_c}{r_i} (r_i^2 + r_c^2)}$$

$$K' = \frac{-2r_c - (r_i^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_i)}}{r_i^2 - r_c^2 + \ln(r_c/r_i)(r_i^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_i)}$$

Experiment Calibration Constant vs Theoretical Constant

The diagonal line corresponds to an exact agreement between the predicted and actual calibration constant for the viscometer. The agreement is quite reasonable for the cylinders with a low calibration constant (slowly falling, larger diameter, closer clearance aluminum cylinders with a small annular gap between the falling cylinder and the inner surface of the quartz tube). For the smaller diameter cylinders, the cylinders fall at a slower rate than expected from theory. This can be attributed to the unstable nature of the fall, as evidenced by these cylinders not falling coaxially through the fluid within the quartz cylinder. One can observe the cylinder wobbling and contacting the quartz cylinder during when these cylinders are employed. Despite this disagreement between the theoretical and experimental values of the calibration constant, the device can still be used to provide an accurate, but not precise, indication of whether substantial increases in carbon dioxide viscosity are occurring.

The vertical line segment is theoretical constant "error bar", because of the variations of the OD of the aluminum cylinder (± 0.00015 inch). The horizontal error bar provides an indication of the variance of the 5-7 readings obtained for the terminal velocity.

4. Results and Discussion

The viscosity results are summarized in the following figure. The viscosity of CO₂ is enhanced 250-fold in 5wt% copolymer-CO₂ solution, and even in 1wt% solution, the viscosity of CO₂ was increased several times. In lower concentration, 0.2wt%, 0.1wt%, there is a discernible viscosity increase. The shear rate and relative viscosity ranges of interest to this project are illustrated by the rectangle in this figure. Although we were not able to obtain data in this region using our falling cylinder viscometer, the extrapolation of the 1.0 and 0.2 wt% results indicate that it may be possible to attain the desired degree of thickening using very dilute concentrations of the polymer.

When viscosity is determined next year using pressure drops for solutions flowing through porous media [17], dilute concentrations (0.1-0.2 wt%) of this copolymer will be employed during the initial tests.

Relative Viscosity vs Shear Rate

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