Synthesis and Evaluation of CO_2 Thickeners Designed with Molecular Modeling

Semi-Annual Report

Start Date: Sept. 1, 2006
End Date: Feb. 28, 2007

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Date Issued: May 7, 2007

DE-FG26-04NT-15533

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Abstract

The objective of this research is to use molecular modeling techniques, coupled with our prior experimental results, to design, synthesize and evaluate inexpensive, non-fluorous carbon dioxide thickening agents. The first type of thickener to be considered is *associating polymers*. Typically, these thickeners are copolymers that contain a highly CO_2-philic monomer, and a small concentration of a CO_2-phobic associating monomer. Yale University will be solely responsible for the synthesis of a second type of thickener; *small, hydrogen bonding compounds*. These molecules have a core that contains one or more hydrogen-bonding groups, such as urea or amide groups. Non-fluorous, CO_2-philic functional groups will be attached to the hydrogen bonding core of the compound to impart CO_2 stability and macromolecular stability to the linear "stack" of these compounds. The third type of compound under investigation is *CO_2-soluble surfactants*. These surfactants contain conventional ionic head groups and composed of CO_2-philic oligomers (short polymers) or small compounds (sugar acetates) previously identified by our research team. Mobility reduction could occur as these surfactant solutions contacted reservoir brine.

In this report, we have elucidated the phase behavior of PLA in CO_2. Previously, we found that low MW PLA was extremely CO_2-soluble but that the solubility was incredibly sensitive to the end groups of the polymer. An examination of previous data by McHugh indicated that very high pressures were required to dissolve very high molecular weight PLA in CO_2. The pressure required to dissolve PLA over the wide MW range bounded by these previous reports has been unknown. With the assistance of Dr. McHugh of Virginia Commonwealth University and Dr. Mark Thies of Clemson University, we have established that amorphous PLA is soluble to at least 5wt% in CO_2 over a very wide range of molecular weight. The pressure required to dissolve PLA in CO_2 increases abruptly at the low MW range, and then quickly levels off over a broad range of MW. Unfortunately, this pressure range of 17,000 – 21,000 psia at ambient temperature is more than twice that required for the dissolution of PVAc. Therefore, PLA will not be pursued further as a viable candidate for CO_2-thickening. PLA is the third most CO_2-soluble polymer that has been identified, however.

This report also highlights our success in designing and synthesizing a very CO_2 soluble polymer with pendant sugar acetate groups. Unlike cellulose triacetate, a highly crystalline CO_2-insoluble polymer with sugar acetates in the backbone, our new polymer has pendant sugar acetates. This novel polymer, poly (1-O-(vinyloxy)ethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside), P(AcGIcVE), is amorphous and capable of readily dissolving in CO_2. Unfortunately, it is slightly less soluble in CO_2 than PVAc. Although it is the second-most CO_2 soluble polymer that has yet been identified, it is not viable for mobility control processes as a polymeric thickener.

This report also details the solubility of tritertbutyl phenol (TTBP) in CO_2. This compound melts in dense CO_2, exhibits extraordinary solubility in CO_2 and is commercially available in bulk quantities at a cost of about $3/lb. The detailed phase behavior of TTBP in CO2 is presented in this report. During the remainder of this research project, we will determine whether this moiety can be successfully integrated into a CO_2-soluble polymer or can be modified top form an associative thickener.

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Executive Summary

In this report, we present a summary of some of our recent work, including new results from the last six months. In particular, we have elucidated the phase behavior of PLA in CO_2. Previously, we found that very low MW PLA was extremely CO_2-soluble (comparable to PVAc) but that the solubility was incredibly sensitive to the end groups of the PLA polymer. An examination of previous data by Mark McHugh indicated that very high pressures were required to dissolve very high molecular weight PLA in CO_2. The pressure required to dissolve PLA over the wide MW range bounded by these previous reports has been unknown. With the assistance of Dr. Mark McHugh of Virginia Commonwealth University and Dr. Mark Thies of Clemson University, we have established that amorphous PLA is soluble to at least 5wt% in CO_2 over a very wide range of molecular weight. The pressure required to dissolve PLA in CO_2 increases abruptly at the low MW range, and then quickly levels off over a broad range of MW. Unfortunately, this pressure range of 17,000 – 21,000 psia at ambient temperature is more than twice that required for the dissolution of PVAc. Therefore, PLA will not be pursued further as a viable candidate for CO_2-thickening. PLA is the third most CO_2-soluble polymer that has been identified, however.

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This report also details the solubility of tritertbutyl phenol (TTBP) in CO_2. This compound melts in dense CO_2, exhibits extraordinary solubility in CO_2 and is commercially available in bulk quantities at a cost of about $3/lb. The detailed phase behavior of TTBP in CO_2 is presented in this report. During the remainder of this research project, we will determine whether this moiety can be successfully integrated into a CO_2-soluble polymer or can be modified top form an associative thickener.

Plans for the Next Reporting Period

PMME, PMEE, PLA, PVAc: No plans other than writing papers about results.

H-Bonding Compounds and Dendrimers: No plans.

CO_2 Soluble Ionic Surfactants: We will complete the study of these compounds and present their effectiveness in stabilizing foam and reducing mobility in core floods. Reid Grigg at NMIMT PRRC was kind enough to assist us with this effort.

PAO: Previously we synthesized PAO, but the characterization indicated that the polymer which branched and did not polymerize in a linear fashion desired for high CO_2 solubility. We will report on our attempts to perform another synthesis of PAO in an attempt to attain a higher purity, more linear, higher molecular weight PAO polymer. We will measure the CO_2 solubility of this new PAO sample.

Polymer with pendant sugar acetate: Our preliminary results have shown that these are the second-most CO_2 soluble polymers that have been identified. Unfortunately, they are less soluble than PVAc. A full report on these results will be presented.

TTBP: We will report on the ability to incorporate TTBP into a thickening compound.

PVAc-styrene copolymer: We will initiate the synthesis of a VAc-sytrene copolymer. We hope that this will be a non-fluorous analog for polyFAST (the fluorinated CO2 thickener). Although we anticipate that the pressure required for dissolution will be too high, we nonetheless want to demonstrate that a non-flourous CO_2 thickener can be synthesized. Hopefully, the vinyl acetate monomer may eventually be replaced by a more CO_2-philic monomer to lower the pressure requirements for dissolution.

Milestones, Decision Points

Our original proposal lists the following decision points and milestones. A review of our progress is provided after each goal.

Decision point for CO_2-CO_2 philic monomer molecular modeling: If the CO_2-novel monomer interactions are weaker than those exhibited by CO_2-vinyl acetate monomer, the monomer will not be considered a viable monomer for polymerization or inclusion in the hydrogen bonding compounds.

To date, we have identified several monomers that exhibit stronger interactions with CO_2 – based on ab initio calculations – than vinyl acetate. These include acetoxy oxetane, methoxy methyl ether, and methoxy ethyl ether. We have been able to qualitatively establish that the interaction of CO_2 with sugar acetates is of comparable strength. This work is completed, with the exception of synthesizing the acetoxy oxetane polymer again because our first sample was not linear or high MW.

Decision point for CO_2 philic polymers: If a polymer less CO_2 soluble than PVAc, it will no longer be considered as a successful advance or a viable candidate.

To date, we have synthesized the monomers and polymers, and have begun testing the solubility of these polymers in CO_2. None of the polymers tested to date, including PMME, PMEE, PAO (low MW, branched) or PLA (over its entire MW range) has been found to be more CO_2-soluble than PVAc. Our final candidates include both a high purity, linear PAO, and a novel polymer with pendant sugar acetate groups. (Preliminary results indicate that the polymer with pendant sugar acetate groups is slightly less soluble in CO_2 than PVAc, however.) This work will be completed during the next six months.

***Decision point for CO_2 thickeners*:** If the co-polymeric thickener or small hydrogen bonding compound cannot increase the viscosity of CO_2 at pressures by a factor of 2-3 at concentrations below 0.5wt%, it will not be considered a success

To date, we have not identified a polymer that is more CO_2-soluble than poly(vinyl acetate) (remember that the pressure required to dissolve high molecular weight PVAc in CO_2 greatly exceeds the MMP, therefore we need a better-than-PVAc polymer), therefore we have not designed new copolymeric thickeners. We have successfully synthesized the first non-fluorous hydrogen bonding compound and dendrimer that are CO_2 soluble, but neither is capable of thickening the CO_2. We anticipate synthesizing and testing a vinyl acetate-sytrene copolymer to prove that CO2 can be thickened with using fluorinated chemicals. It is extremely unlikely that this copolymer will dissolve at pressures near the MMP.

***Milestone 1*:** The identification of oxygenated hydrocarbon monomers that interact more favorably with CO_2 (according to molecular modeling) than vinyl acetate

We have successfully attained this target and have completed the synthesis of novel polymers based on these modeling results.

***Milestone 2*:** The synthesis of novel oxygenated hydrocarbon polymers that are more CO_2 soluble than poly(vinyl acetate).

None of the proposed polymers were more CO_2 soluble than PVAc. PMME, PMEE, PAO and PLA are less CO_2 soluble than PVAc. Preliminary results for a high molecular weight polymer with pendant sugar acetates indicate that it is slightly less CO_2 soluble than PVAc. A high purity, linear PA is currently being synthesized.

***Milestone 3*:** The synthesis of novel oxygenated hydrocarbons that can dissolve in CO_2 at pressures at or below the MMP

Because none of the polymers made during this project is more CO_2 soluble than PVAc, we have not achieved this goal. (Milestone 2 must be successfully achieved prior to approaching this milestone). We have identified several small compounds that are extraordinarily CO_2 soluble, such as tritertbutyl phenol, but have yet to be able to incorporate it into a thickener or polymer.

***Milestone 4*:** The synthesis of novel oxygenated hydrocarbon thickeners (copolymers or small H-bonding compounds) that can dramatically increase the viscosity of CO_2 by a factor of 2-20 at a concentration of 0.1-0.25wt% at pressures at or below the MMP.

We have successfully designed the first CO_2 soluble, non-fluorous hydrogen bonding compound and non-fluorous dendrimer. Unfortunately, neither appears to be soluble at conditions close to reservoir temperature and MMP, and neither appears to be capable of thickening CO_2 even at elevated pressure. We will synthesize and test a vinyl acetate-styrene copolymer to determine if a non-fluorous thickener can be synthesized (even though it is unlikely to dissolve at the MMP).

Previously we have designed a possible new type of CO_2 thickener; CO_2 soluble ionic surfactants that may be capable of generating CO_2 foams in-situ. Dr. Reid Grigg of NMIMT has determined the mobility of these solutions in brine-saturated cores. His results will be presented in the next report.

Significant Accomplishments

In our *previous* four reports, we detailed the following significant accomplishments:

The design, synthesis and characterization of the first polymer designed for CO_2-solubility using molecular modeling, *poly(methoxy methyl ether), PMME.*

The design and synthesis of the second polymer designed using molecular modeling, *poly(3-acetoxy oxetane), PAO*. Ab initio calculations indicate that PAO has the greatest interactions with CO_2 of any polymer composed of C, H and O that we have considered to date.

The design, synthesis and characterization of the first series of non-fluorous, ionic, highly CO_2-soluble surfactants that has been reported. (These surfactants, which would be dissolved in CO_2, may be able to form mobility control foams in-situ as the CO_2-surfactant solution mixes with the brine already in the reservoir.) Specific tails include oligo(vinyl acetate), sugar acetates, and oligo(propylene oxide). The surfactants with vinyl acetate tails were particularly promising.

The first observations of CO_2 foams generated by mixing of CO_2, water and a CO_2-soluble surfactant. Specific tails include oligo(vinyl acetate), sugar acetates, and oligo(propylene oxide). The surfactants with vinyl acetate tails were particularly promising.

The phase behavior of the two novel polymers designed with molecular modeling: PMME and low MW branched PAO.

The first report of a highly CO_2-soluble, non-fluorous hydrogen-bonding compound, and the first report of a non-fluorous dendrimer designed for solubility in CO_2. Unfortunately, neither of these compounds was capable of dissolving at pressures low enough to make them viable candidates for potential CO_2 thickeners. Further, there were no preliminary indications that either compound was thickening the CO_2 even at elevated pressure.

Technology Transfer

The results associated with this work have been published in (or submitted to) the following journals.

Oxygenated Hydrocarbon Ionic Surfactants Exhibit CO_2 Solubility, Fan, X.; Potluri, V. K.; McLeod, M. C.; Wang, Y.; Liu, J.; Enick, R. M.; Hamilton, A. D.; Roberts, C. B.; Johnson, J. K.; Beckman, E. J.; *Journal of the American Chemical Society;* (Article); 2005; *127*(33); 11754-11762

Sevgi Kilic, Stephen Michalik, Yang Wang, J. Karl Johnson, Robert M. Enick, Eric J. Beckman, "Phase Behavior of Oxygen-Containing Polymers in CO_2", *Macromolecules* 40 (4): 1332-1341 FEB 20 2007

Fan, X.; Mcleod, M. C.; Enick, R. M.; Beckman, E. J.; Roberts, C. B. Preparation of Silver Nanoparticles via Reduction of a Highly CO_2-Soluble Hydrocarbon-Based Metal Precursor. *Industrial & Engineering Chemistry Research*. (In press)

Bell, P. W.; Anand, M.; Fan, X.; Enick, R. M.; Roberts, C. B. Stable Dispersions of Silver Nanoparticles in Carbon Dioxide with Fluorine-Free Ligands. *Langmuir* 2005 21, 11608-11613.

Eastoe, J., Gold, S., Rogers, S., Wyatt, P., Steytler, D., Gurgei, A., Heenan, R., Fan. X., Beckman, E., Enick, R., Designed CO_2-philes Stabilized Water-in-Carbon Dioxide Microemulsions, *Angewandte Chemie International Edition*, 2006, ON 1521-3773, PN: 1433-7851

Synthesis and Steric Stabilization of Silver Nanoparticles in Neat CO_2 Solvent Using Fluorine-Free Compounds, Madhu Anand, Philip W. Bell, Xin Fan†, Robert M. Enick†, Christopher B. Roberts (submitted to JACS)

Yang Wang, Lei Hong, Inchul Kim, Jacob Crosthwaite, Andy Hamilton, Mark Thies, Eric J. Beckman, Robert M. Enick, J. Karl Johnson, Design and Evaluation of Non-fluorous CO_2-Soluble Polymers, submitted to Macromolecules

Ik-Hyeon Paik, Deepak Tapriyal, Robert Enick, Andrew Hamilton, Highly CO_2-Soluble Dendrimers and Bis-Urea Hydrogen-Bonding Compounds, submitted to Angewandte Chemie International Edition

Tri-tert-butylphenol: a Highly CO_2-Soluble Sand Binder

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ABSTRACT

Tri-tert-butylphenol (TTBP) holds great promise as a CO_2-recyclable sand binder. TTBP powder can be easily combined with sand, heated to at least its melting point (400 K) and then cooled to form rigid molds for metal forming operations. Further, TTBP exhibits significant melting point depression in the presence of dense CO_2 and very high solubility in liquid and supercritical CO_2 These properties facilitate the separation of TTBP from used molds via dissolution into dense CO_2 and its subsequent recovery – via depressurization – for reuse. Pressure-composition diagrams at 301, 328 and 343 K indicate that TTBP is about 18, 50 and 70wt% soluble in dense CO_2, at pressures above 8, 14 and 16 MPa, respectively. At each temperature, the solubility of TTBP decreased slightly when pressure was increased above roughly 50 MPa. The TTBP-rich liquid phase composition at three-phase (SLV) equilibrium pressures of 6.75, 9.76 and 9.24 MPa at 301, 328 and 343 K is 8, 52 and 70 wt% TTBP, respectively.

Keywords: Tri-tert-butylphenol; Sand binders; Phase behavior; Supercritical CO_2; Melting point depression

Introduction

There has been much recent progress in the identification of non-fluorous, highly CO_2-soluble small compounds, oligomers and polymers for chemical and petroleum engineering applications. For example, poly(vinyl acetate), PVAc, has been identified as the most CO_2 soluble high molecular commodity polymer.[1,2] Oligomers of vinyl acetate have also been employed as the CO_2-philic segment of ionic and non-ionic surfactants.[3-5]. Sugar acetates, including glucose acetate, galactose pentaacetate, maltose octaacetate and acetylated cyclodextrins have also been shown to exhibit very high solubility and significant melting point depression in CO_2 [6-9] These CO_2-philic compounds have been evaluated as the CO_2-philic segments of surfactants, copolymers and nano-particle precursors.

It has been recently proposed that CO_2-soluble solids may be viable candidates for a recyclable (via supercritical CO_2 extraction) sand binder for metal forming operations. [10,11] In one version of forming a mold, the binder particles are mixed with sand, heated until the binder melts, and then cooled to solidify the binder. This process forms a rigid mold that retains a cavity into which the molten metal is poured and then allowed to solidify. In powder injection molding, the binders are combined with ceramic powders to form a paste that is injection molded into the desired shape. In both processes, after the desired metallic or ceramic solid product has been formed, the binders are removed by combustion, thermal debinding or solvent extraction. Each of these processes has significant environmental concerns. It is our intent to develop a CO_2-based, sustainable technique for the recovery and re-use of both the binder and the sand.[11] After being used in the metal forming operation, small fragments of the used mold would be immersed liquid or supercritical (sc) CO_2 retained at pressures preferably no greater than 20 MPa within in an agitated vessel.

Dissolution of the binder from the matrix into the sc-CO_2 would be facilitated and hastened by compounds exhibiting a significant melting point depression (which would allow a binder-rich, low viscosity liquid phase to drain from the broken mold pieces) and a high solubility of the binder in the high pressure CO_2. The CO_2-binder solution could then be displaced to another vessel, where the binder and CO_2 could be separated via depressurization and then recovered for reuse.

CO_2-soluble high molecular weight oxygenated hydrocarbon-based polymers are not viable candidates for sand binding at the relatively low pressures of 20 MPa or less. Pressures of roughly 70 MPa or more are required to dissolve several weight percent of PVAc, for example. Therefore Manke and co-workers evaluated a small CO_2-philic compound, β-D-galactose pentaacetate (GPA) and found that high solubility values of this compound in CO_2 could be realized along with significant melting point depression at much more reasonable pressures than those required to dissolve polymers. GPA can form a single-phase solution in CO_2 at concentrations as high as 25wt% at mild conditions, 10.3 MPa at 308 K and 15.7 MPa at 323K. Small sand plugs, roughly 1 cm^3 in volume bound with GPA completely filling the voids between the sand required about five minutes to completely disintegrate in the dense CO_2. Although this was a promising proof-of-concept result, GPA is not stable when subjected to repeated heating/cooing cycles in the presence of humid air. Therefore sugar acetates do not appear to be commercially viable for this process [10].

Manke and co-workers also explored the use of 1,3,5-tri-tert-butylbenzene (TTBB) as a sand binder. The use of TTBB and other tert-butylated aromatic compounds was suggested by

Rodger Marentis who had previously conducted a proprietary supercritical fluid study in which these were utilized as one of the candidate reactant compounds. He was surprised to find that these compounds were incredibly CO_2-soluble and also noted that at room temperature (in the absence of CO_2) many of these compounds formed a very hard solid. He realized that these properties made TTBB and other tert-butlyated compounds promising sand binder candidates. Manke and co-workers confirmed that TTBB exhibited extremely high CO_2-solubility, significant melting point depression and very rapid drainage of TTBB from the sand plug at ambient temperature[12]. The sand plugs disintegrated in less than a minute, a much shorter time than that required for the disintegration of the GPA-bound sand plugs. Unfortunately, TTBB is extremely expensive and there are no commercial suppliers of TTBB (only small research-scale quantities are available). Therefore TTBB is not considered to be a commercially viable sand binder.

The objective of this study was to determine the phase behavior of another CO_2 sand binder candidate [10], a tert-butylated aromatic compound, 2,4,6-tri-tert-butylphenol (TTBP). Unlike TTBB, TTBP has been commercially available in very large amounts at a price of several dollars per pound. Further, qualitative observations of sand plugs bound with TTBP indicate that they are as resilient as plugs formed with either GPA or TTBB, but the dissolution rate of the TTBP into CO_2 was slower than that of TTBB or GPA at comparable conditions. Heating of the CO_2/TTBP-bound sand plug system to about 323 K was required for the sand plug to disintegrate within several minutes.[11]

This study will examine the phase behavior of CO_2-TTBP mixtures in an attempt to identify the temperature and pressure conditions at which the CO_2-based recycling process may be effective.

Experimental

Materials

2,4,6-tri-tert-butylphenol (96%, TTBP) was obtained from TCI and recrystallized with a methanol and water mixture before use. CO_2 was purchased from Penn Oxygen (Coleman Grade 99.99%). The structure and physical properties of the TTBP are shown in Figure 1 and Table 1, respectively.

Phase Behavior Measurement

A standard non-sampling technique, also known as the synthetic method, was employed for generating the phase behavior diagrams.[2,7,8] Bubble-point, dew-point, cloud point, and three-phase loci were determined by isothermal compression and expansion of binary mixtures of known overall composition. At these elevated-pressure conditions, either a transparent liquid phase (at lower overall concentrations of the solid in CO_2) or solid-liquid equilibrium was observed. The sample volume was then slowly expanded, and the pressure values associated with the appearance of an additional phase were recorded. Bubble points were characterized by the co-existence of a minute amount of vapor phase in equilibrium with the liquid phase. Dew points were designated as the pressure at which it was no longer possible to see through the solution (after maintaining the sample volume under quiescent conditions for 30-60 min, several drops of liquid would accumulate at the bottom of the sample volume). For some high pressure single-phase solutions containing high

concentrations of TTBP, *increases* in pressures to very elevated values also resulted in cloud point occurrences.

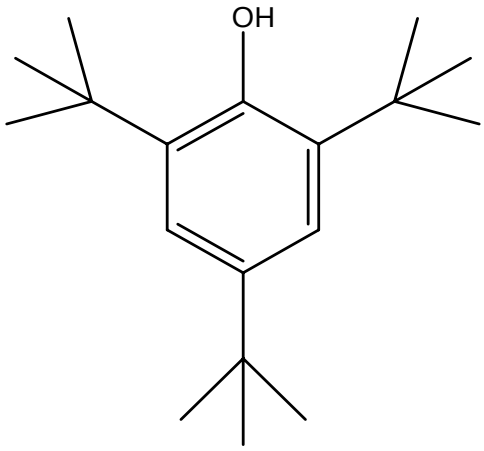


Figure 1 Structure of 2,4,6-tri-tert-butylphenol, TTBP, $C_{18}H_{30}O$

Table 1 Physical properties of tri-tert-butylbenzene. Octadecane data provided for comparison of TTBP with n-octadecane a linear alkane that has the same number of carbons.

Compound	Formula	Molecular Weight (g/mol)	Melting Point (K)	Boiling Point (^oC)
2,4,6-tri-tert-butylphenol (TTBP)	$C_{18}H_{30}O$	262.43	398-403	550
n-octadecane	$C_{18}H_{38}$	254.49	299-302	590

Results and Discussion

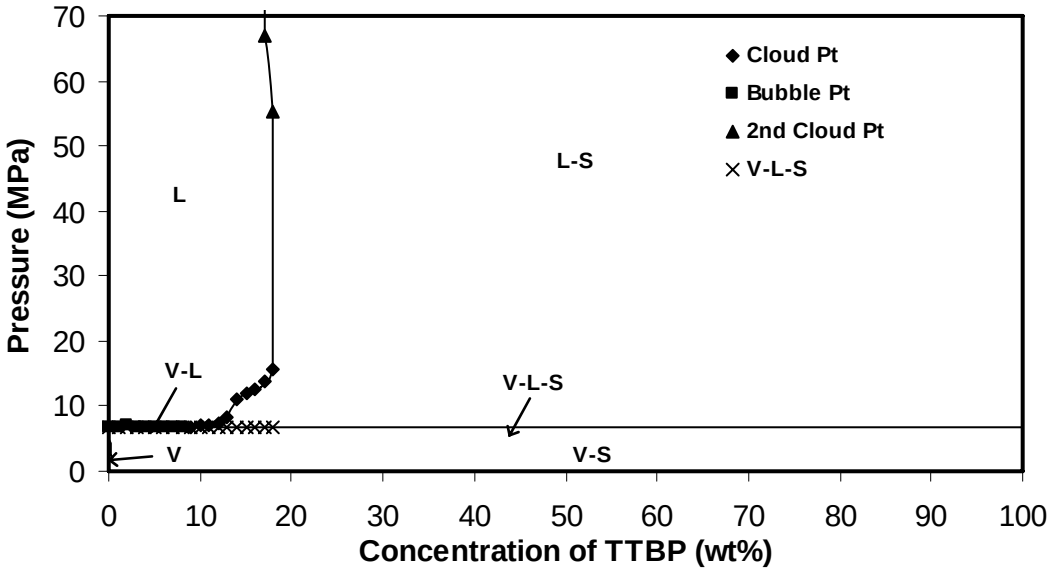
Pressure-composition diagrams for mixtures of CO_2 and TTBP at 301K, 328K, and 343K are presented as isotherms in Figure 2, Figure 3, and Figure 4. The solubility of the TTBP in CO_2 is extremely high relative to linear hydrocarbons with an equivalent number of carbon atoms, such as octadecane, Table 1. The solubility of n-octadecane is only several weight percent at 310, 313, 333, and 353K and pressures up to 20 MPa.[13] However, the TTBP concentration in the liquid (L) phase at the CO_2/TTBP mixture at the vapor-liquid-solid (VLS) pressure is 8.5wt%, 52wt% and 70wt% at 301K, 328K and 343K, respectively. The maximum solubility of TTBP in CO_2 in the single phase L region at 301K, 328K and 343K is about 18%, 52wt%

and 70wt%, respectively. The mixture critical point at the two supercritical temperatures, 328K and 343K, occurred between 20-25wt% TTBP. At all the three temperatures, increasing pressure eventually diminished solubility of the nearly saturated single-phase solutions of TTBP in CO_2. For example, at 343 K a 65wt% mixture of TTBP in CO_2 enters the single phase region as pressure is increased to 12 MPa, single phase behavior is maintained between 12 and 52 MPa, but further pressure increases lead to the re-appearance of a cloud point with TTBP in the form of small particles.

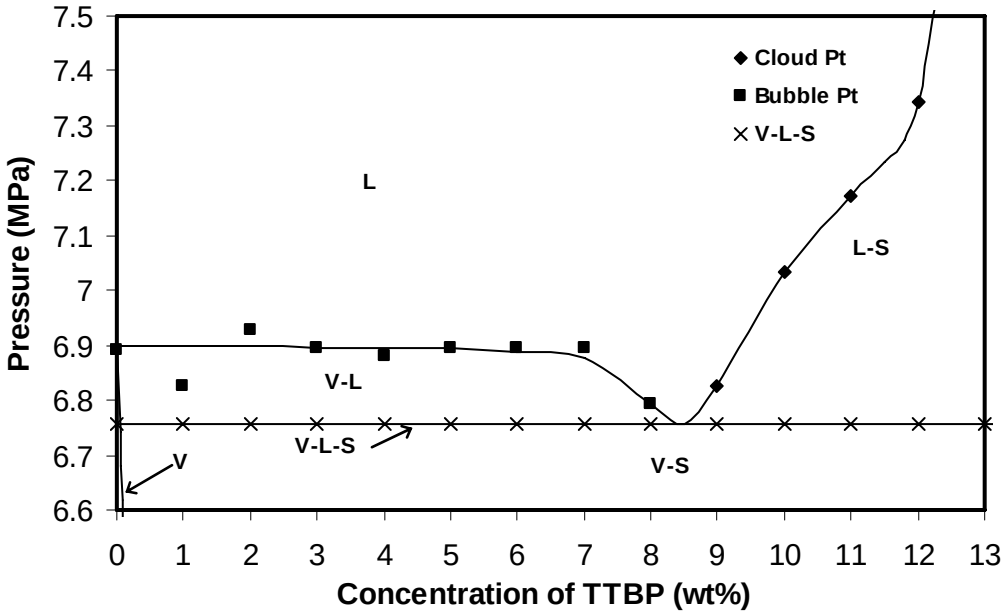
A quantitative measure of the melting point depression of TTBP in dense CO_2 as a function of the composition of the molten TTBP phase at three phase equilibrium conditions is shown in Figure 5 (A similar diagram has been recently presented for the CO_2-TTBB system reference. [12]) The melting point of neat TTBP, 400K, is denoted on the y-axis at 0% CO_2. The temperatures associated with the three isothermal Px diagrams is also plotted against the CO_2 concentration in the TTBP-enriched liquid phase L at the three-phase pressure at the corresponding temperature. The melting point depression is demonstrated in Figure 5 in which the melting point is plotted versus two variables: the wt% of CO_2 in the TTBP-enriched liquid phase at three-phase equilibrium conditions, and the three phase equilibrium pressure. As expected, greater concentrations of CO_2 in the TTBP-rich liquid phase were associated with lower temperature values (greater melting point depression). The three phase equilibrium pressure values represent the minimum pressure required for melting point depression. This pressure value increased and then decreased with increasing temperature, which was not unexpected in light of the shape of the SLV locus in Figure 6, which reaches a maximum value as temperature increases before decreasing and then terminating at the TTBP triple point.

These pressure-compositions diagrams can be used to generate a semi-quantitative description of the global phase behavior of the CO_2/TTBP system, presented in Figure 6. Points C_1 and C_2 represent critical points of CO_2 and TTBP, respectively (Tc,CO_2= 304.13K, Pc,CO_2=7.38MPa; critical point data for TTBP are not available). M is the triple point of TTBP, and the triple point temperature was estimated from the normal melting point value. Curves AC_1 and MC_2 are the pure component vapor pressure curves of CO_2 and TTBP, respectively. Curve MN is the TTBP melting curve, and curve DM corresponds to the TTBP sublimation curve. The three pressure-composition isotherms shown in Figure 2, Figure 3, and Figure 4 correspond to the three dashed lines a, b, and c in Figure 6 at 301K, 328K, and 343K, respectively. From the one-phase region to lower pressures, isotherm "a" in Figure 6 intersects in order the CO_2 vapor pressure curve at 6.87 MPa, and then crossing VLS three-phase line. Similarly, isotherm "b" and "c" have intersections with the critical mixture curve, DH, and VLS three-phase line (We denote liquid phase as fluid phase when the temperature is higher than the CO_2 critical temperature.). The VLS equilibrium pressure was identified as 6.76 MPa at 301 K. The three phase equilibrium pressure increased with the increase of temperature. At 328K three-phase VLS line was observed 9.75 MPa. However, the VLS equilibrium pressure started decreasing after it reached the maximum value. As shown in Figure 6 the VLS equilibrium was obtained at 9.24 MPa at 343 K. Nonetheless, the mixture critical point (~16.89 MPa) at 343 K is higher than that (~12.82 MPa) at 328 K. This P-T projection is proposed merely based on the phase behavior data on three temperatures we discussed in the paper (301K, 328K, and 343K). Therefore, the shapes of the mixture critical point curve and VLS curve above 343K are qualitative representations. Based on our observation, we propose that the fluid-phase behavior is Type I according to the classification

system of Scott and Van Konynenburg because both critical mixture curve (C_1C_2 in Figure 6) and three-phase vapor-liquid-solid (BM in Figure 6) locus are continuous in the temperature range that we explored[14,15].



(a)



(b)

Figure 2 Pressure –composition diagram for CO_2 +TTBP system at 301K, (a) aN overall view, (b) a view of the lower TTBP concentration region

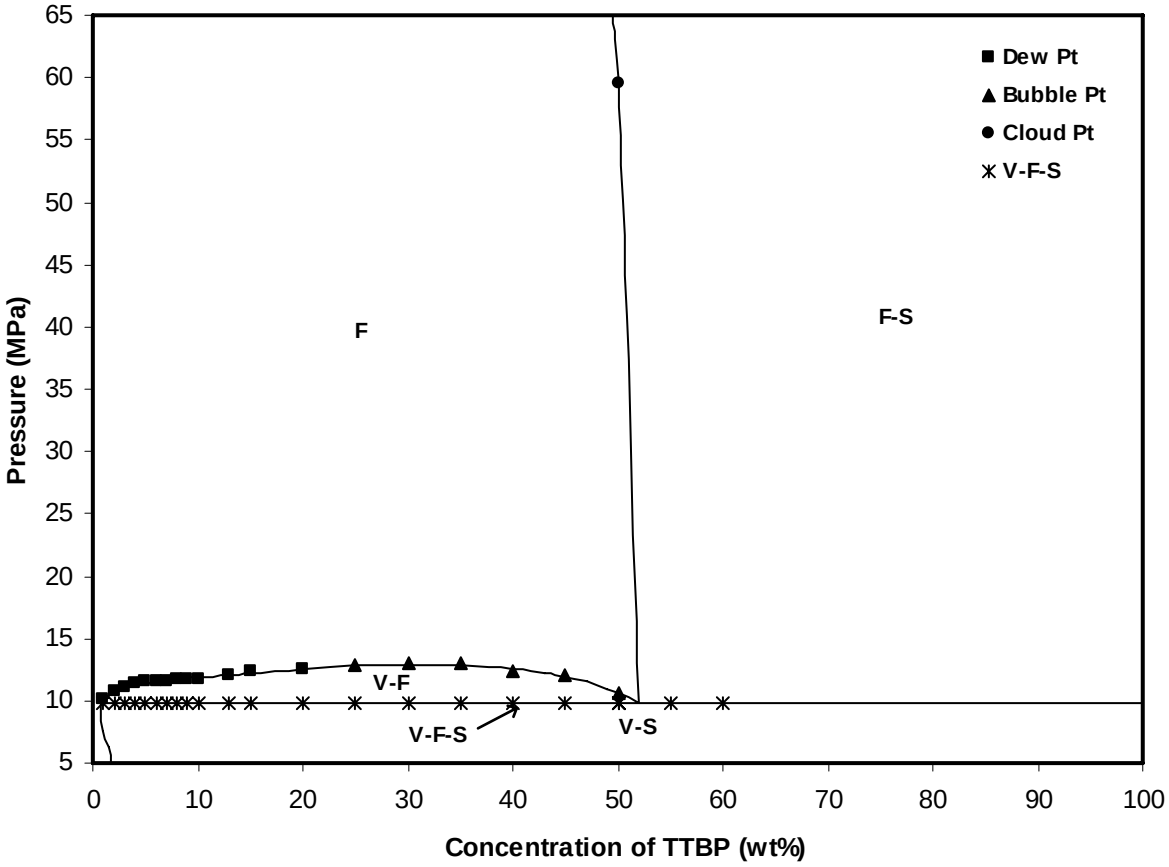


Figure 3 Pressure –composition diagram for CO_2 +TTBP system at 328K

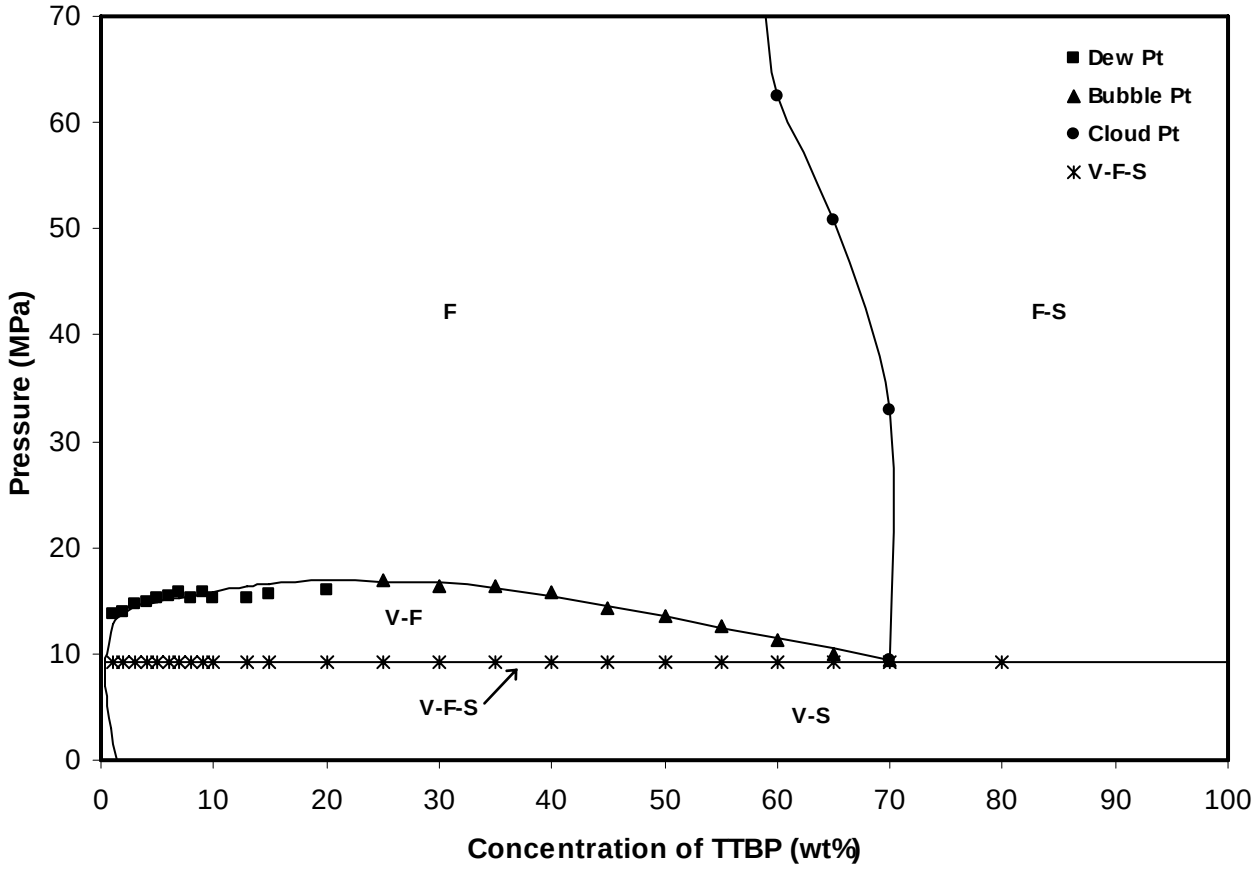


Figure 4 Pressure –composition diagram for CO_2 +TTBP system at 343K

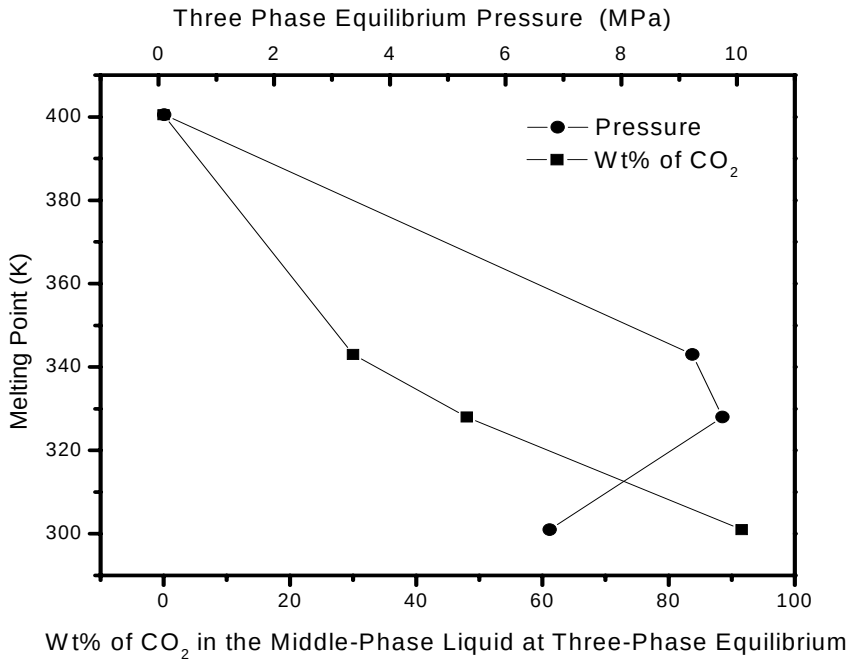


Figure 5 Melting point depression of TTBP in CO_2. The lower x-axis represents the CO_2 content of the middle-phase liquid at three-phase equilibrium. The upper x-axis represents the corresponding VLS equilibrium pressure

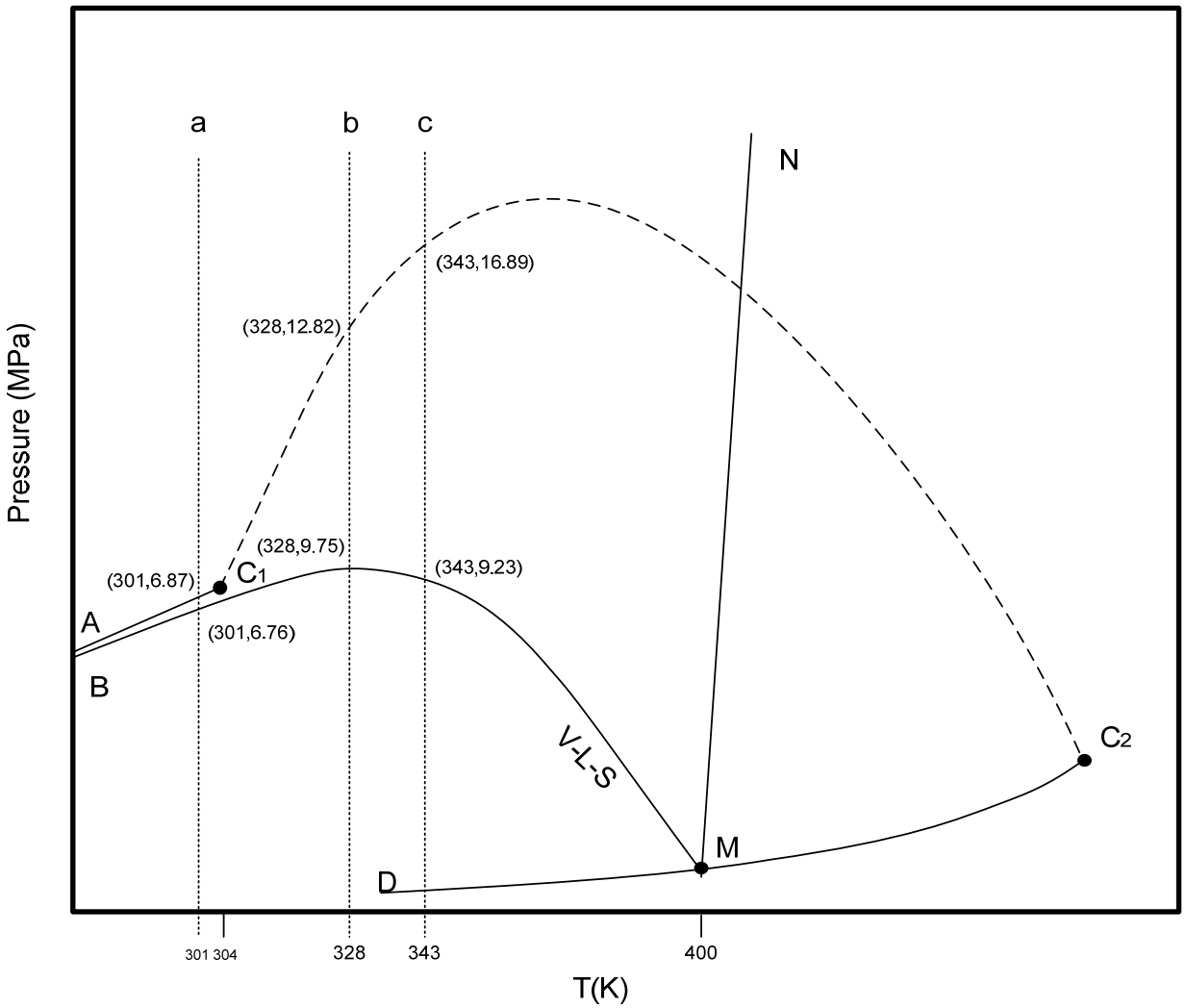


Figure 6 P-T diagram for CO_2+TTBP system; C_1 and C_2 represent critical points of CO_2 (TC,CO_2 = 304.13 K, PC,CO_2 = 7.38 MPa) and TTBP, respectively; M is the triple point of TTBP; AC_1 is CO_2 vapor pressure curve; MN and DM are TTBP melting curve and sublimation curve, respectively; BM is three-phase solid-liquid-vapor line; C_1C_2 is the mixture critical curve.

Conclusions

The phase behavior of tri-tert-butylphenol (TTBP) in dense CO_2 was investigated at three temperatures in order to assess its viability as a CO_2-recyclable sand binder. The results indicated that TTBP has several desirable attributes for this application, including significant melting point depression and very high solubility of TTBP in dense CO_2 at pressures below 20 MPa. All the three isotherms are characterized by a VLS (VFS) three phase equilibrium line, a VL (VF) two phase equilibrium region, and a LS (FS) two phase equilibrium region, and a VS two phase equilibrium region. The VL (VF) region expands with the increase of temperature or the temperature range studied, revealing the very high solubility of TTBP in dense CO_2. The three phase equilibrium lines were determined at 6.76MPa, 9.76MPa, and 9.23MPa at 301K, 328K and 343K, respectively. The TTBP-rich liquid phase composition at three phase equilibrium conditions is 7.5wt%, 52wt%, and 70wt% at 301K, 328K, and 343K, respectively. The mixture critical points were 12.82MPa and 16.89MPa at 328K and 343K, respectively. A P-T diagram of the CO_2-TTBP mixture exhibited System type I behavior according to the classification by Scott and Konynenberg.[14] Remarkably, TTBP contains no CO_2-philic oxygenated hydrocarbons functionalities, such as acetate[6,16,17] and ether[18], commonly associated with highly CO_2 soluble compounds. In fact, the hydroxyl group is known to be CO_2-phobic. Yet TTBP exhibits incredible CO_2 solubility relative to a linear hydrocarbon with the same number carbons, octadecane. Apparently, the highly branched perimeter of the TTBP structure is able to enhance the CO_2 solubility through weakening the interaction forces among solute molecules.

Acknowledgments

The authors express thanks to Dr. Manke, Dr. Gulari, and Dr. Dilek from Wayne State University for their many useful discussions of the phase behavior. Thanks also go to Bob Richardson, Account Mgr - Chemical Division, SI Group (Formerly Schenectady International) for discussions concerning the manufacture of TTBP. We are grateful for support from the U.S. Environmental Protection Agency Grant EPA-RD-83150401-1. The project was also supported in part by US DOE NETL (DE-PS26-04NT15450-0).

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Non-fluorous, CO_2-philic Polymers, Oligomers and Small Compounds for Chemical and Petroleum Engineering Applications

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In an attempt to enhance the performance of supercritical carbon dioxide, $scCO_2$, as a processing fluid for chemical and petroleum engineering applications, there has been an on-going effort to develop new CO_2-soluble polymers, oligomers, dispersants chelating agents, catalysts and surfactants which could enhance the potential of CO_2 as a processing fluid[i,ii,iii].We have drawn our attention to the identification of highly CO_2 soluble oligomers because they can be incorporated as the CO_2-philic group/segment in surfactants, dispersants chelating agents, dendrimers, hydrogen bonding compounds, polymers, co-polymers or thickeners. Further, in an attempt to mitigate high costs and environmental and health concerns, non-fluorous compounds will be investigated.

Polymers

It has been previously demonstrated[iv] that polymers possessing electron-donating functional groups display Lewis acid-base interaction in carbon dioxide with carbonyls, acetates and ethers. McHugh et al were the first to note that poly(vinyl acetate) (PVA) exhibited a significantly greater solubility in CO_2 than a lower molecular weight sample of poly(methyl acrylate) despite the two polymers beings isomers [v]. The subsequent study of Enick, McHugh and co-workers that investigated the solubility of PVAc over a very wide range of molecular weight confirmed that this polymer is the most CO_2-soluble, oxygenated

hydrocarbon, high molecular weight polymer that has yet been identified[vi]. The favorable thermodynamic interaction is between the carbon of CO_2 which acts as Lewis acid and the oxygen present in the side chain of the polymer which acts as Lewis base and hydrogen bonding between the O of the CO_2 and a proton on the methyl group[vii] (C-H…O) may be responsible for high solubility of poly(vinyl acetate) in CO_2. In this paper we evaluated a novel polymer, which was rich in sugar acetates, to determine if it was also CO_2-soluble.

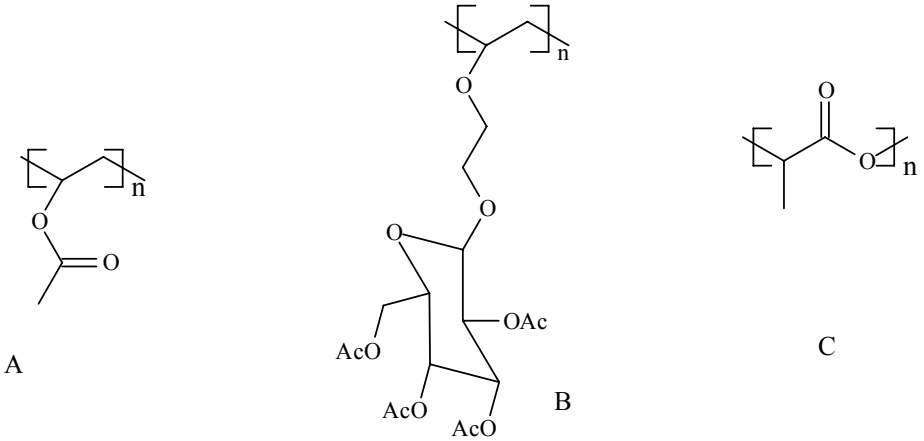


Figure 7: - A) Poly(vinyl acetate), B) poly(AcGIcVE), C) Poly(lactic acid)

We have previously[viii,ix] shown that peracetylated sugar molecules exhibit high solubility in CO_2. However cellulose triacetate, which is linear chain of peracetylated sugar molecules, was crystalline and, not surprisingly, insoluble in CO_2. So we synthesized[x] poly (1-O-(vinyloxy)ethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (poly(AcGIcVE), Figure 1, which has peracetylated sugar molecules as a pendent group (rather than a backbone unit). This polymer has a low melting point, 50°C, and was remarkably CO_2-soluble. Its phase behavior in CO_2 showed that 5 wt% is soluble in CO_2 at 74 MPa. Currently, it is second-most CO_2 soluble high molecular weight polymer. Figure 2 shows the comparison of cloud points of mixtures of CO_2 and PVAc, and also mixtures of CO_2 and poly(AcGIcVE).

Although McHugh's prior work on high molecular, amorphous weight poly(D-L lactic acid), PLA[xi], demonstrated that is was less CO_2-soluble than PVAc, PLA has much better mechanical properties (e.g. higher melting point) than either PVAc or poly(AcGIcVE). Therefore we established the CO_2 solubility of PLA (derived from a racemic mixture of the D and L monomers to yield a non-crystalline polymer) over a wide range of molecular weight. The cloud point pressure for mixtures of 5wt% PLA and 95% CO_2 are more than twice as great as those for mixtures of CO_2 and PVAc.

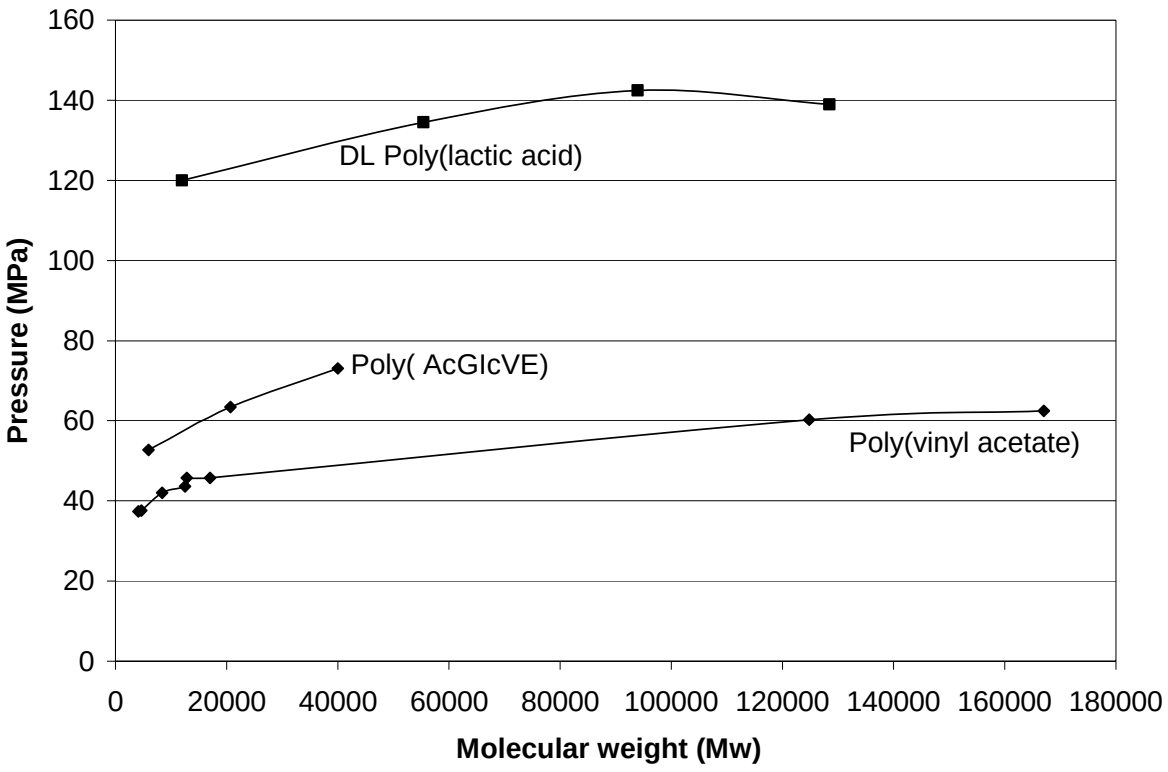
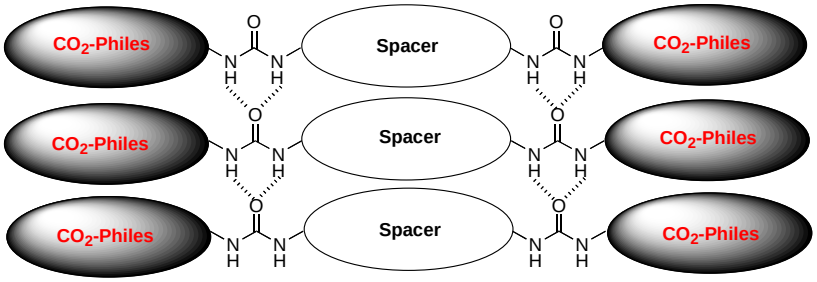


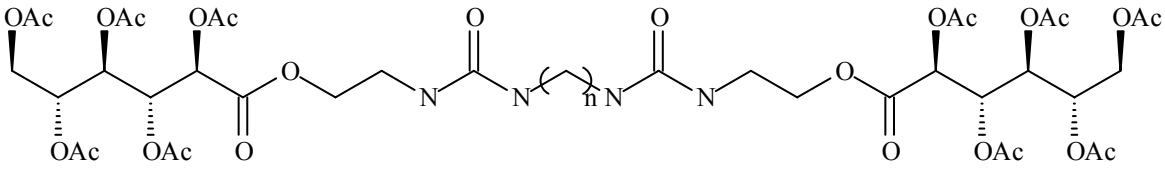
Figure 8: - Cloud-point pressures at 5 wt% polymer concentration and 298 K for binary mixtures of CO_2 with PVAc, P(AcGIcVE) and amorphous PLA as a function of weight average molecular weight.

Hydrogen bonding compounds

We have previously shown that self-aggregating organic compounds containing both hydrogen bonding urea groups and fluorinated CO_2-philic tails could modestly increase the viscosity of $scCO_2$.[xii] Upon depressurization these solutions produced free-standing foams which represent organic analogs of silicate aerogels with sub-micron sized fibers and a bulk density reduction of greater than 90% of the parent material. A critical feature of these small, self-assembling molecules is the presence of strong and directional hydrogen bonding interactions between carbonyl oxygen and hydrogen in urea or bis-urea moiety in each molecule (Figure 3a). These molecules can interact with each other and thus form viscosity enhancing polymeric structures through non-covalent interactions in solutions, and free-standing foams upon the removal of the CO_2. Non-fluorous hydrogen-bonding compound, Figure 3a, was synthesized which dissolved in CO_2 and similarly self-associating to form novel materials.



a

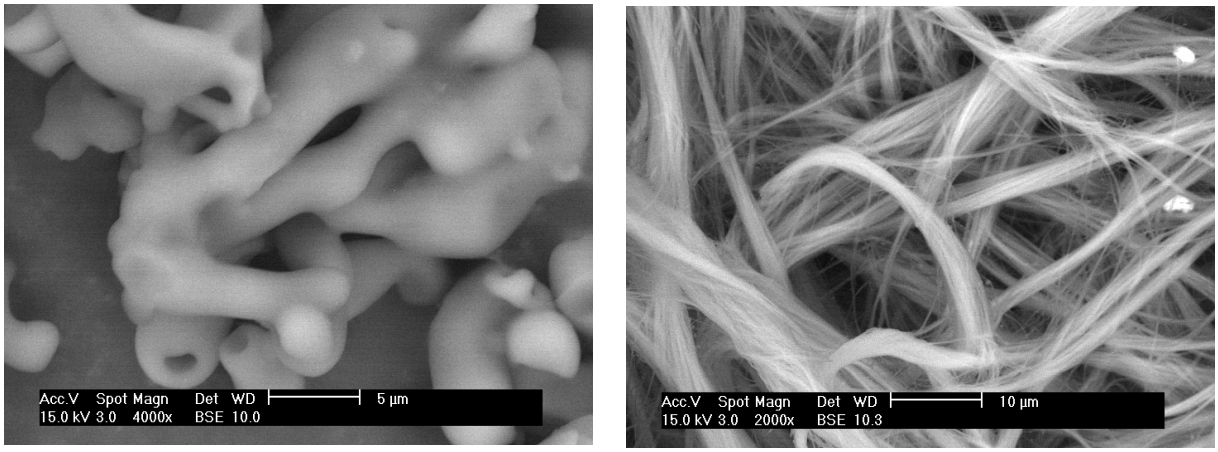


b (n = 4)

c (n = 6)

Figure 9: - (a) Intermolecular hydrogen bonded network of bis-ureas with CO_2-philes (b) Bis-ureas with two highly acetylated arms

At 298 K 3b (typically powder) could dissolve in CO_2 at pressure of 62 MPa at 1 wt % and compound 3c (typically powder) at 65 MPa at 1 wt %. The single phase, transparent solution attained at these conditions (e.g. 65 MPa, 298 K, 1wt% of compound 3b) was apparently meta-stable. After 2-5 minutes, a small amount of very fine fibers began to form in the solution. Apparently, at isothermal and isobaric condition, the dissolved compounds began to hydrogen bond and associate, resulting in the macromolecules coming out of solution in the form of fibers. Within 20 minutes the sample volume was filled with fibers. Upon the removal of CO_2, very brittle, free-standing, micro-fibrillar foam formed, with an average fiber diameter of 1-3 microns. SEM images of the fibrous material obtained is shown in Figure 4, along with the morphology of the powder sample before the addition of CO_2. At ambient temperature, foam produced has major fiber diameter of 1-3 microns, with these fibers being composed of sub-micron fibers, and had higher porosity than at low temperature.



A B

Figure 10: - SEM image of compound before introduction of CO_2 (A), and the fibers formed at elevated pressure at 25ºC (B)

CO_2-Soluble Dendrimer

Due to the promising results associated with the hydrogen-bonding compound, a first generation dendrimer containing four CO_2-philic highly acetylated arms with bis-urea core, shown in Figure 5, was synthesized at Yale University. It was soluble in CO_2 foam 1-5 wt % in liquid CO_2 at 25ºC as well as in supercritical CO_2 at 44ºC as shown in Figure 21a, a P-x isotherm. These results constitute a small portion of the overall phase P-x diagram of this binary, which is illustrated in Figure 6. These are the first CO_2-soluble dendrimers that we are aware of that are composed solely of C, O, H and N. Unlike the linear, hydrogen-bonding compounds discussed earlier, this dendrimer formed a powder, not rigid fibrous foam, upon the removal of CO_2. Viscosity measurements have not yet been made on this compound. It is unlikely that significant H-bonding is occurring because the compound melted immediately in dense CO_2 and upon depressurization no fibers formed.

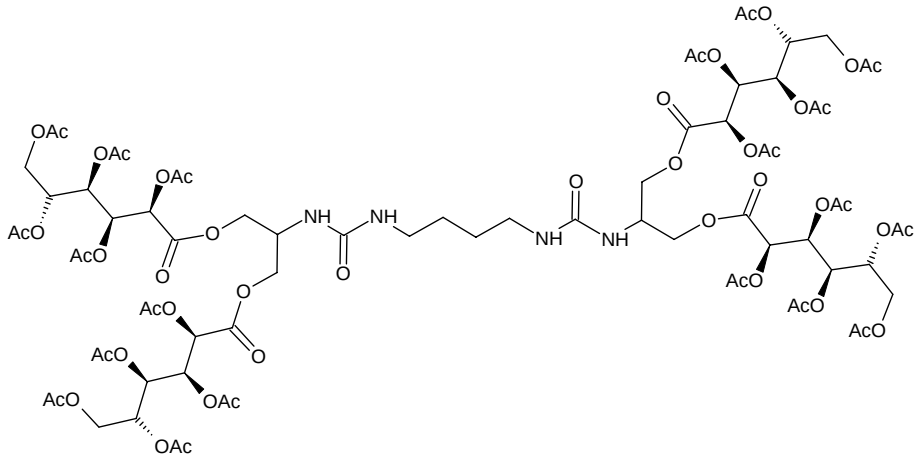


Figure 11: CO_2-soluble dendrimer solely made of C, O, H and N.

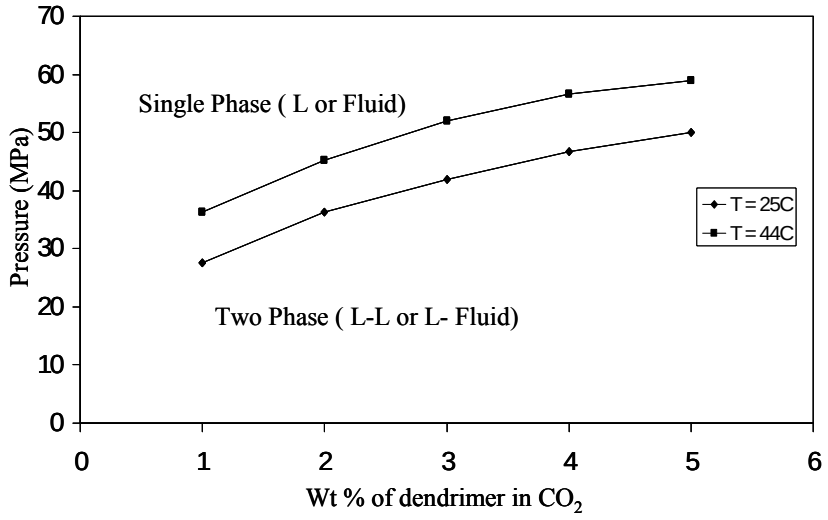


Figure 12: - Cloud point curve of dendrimer in CO_2 at different temperature.

Cellulose Triacetate Oligomers

Cellulose triacetate, CTA, is insoluble in $scCO_2$. Our group and others have studied the phase behavior of various small peracetylated sugar compounds in CO_2. A monosaccharide, β-D-galactose pentaacetate, was very soluble in CO_2, as was maltose octaacetate, a per-acetylated disaccharide. In an attempt to determine the CO_2 solubility of longer per-acetylated sugars, peracetylated oligomers were synthesized by a degradation method, the pivaloylysis of CTA[xiii] shown in figure 3. Higher molecular weight oligomers are currently being synthesized.

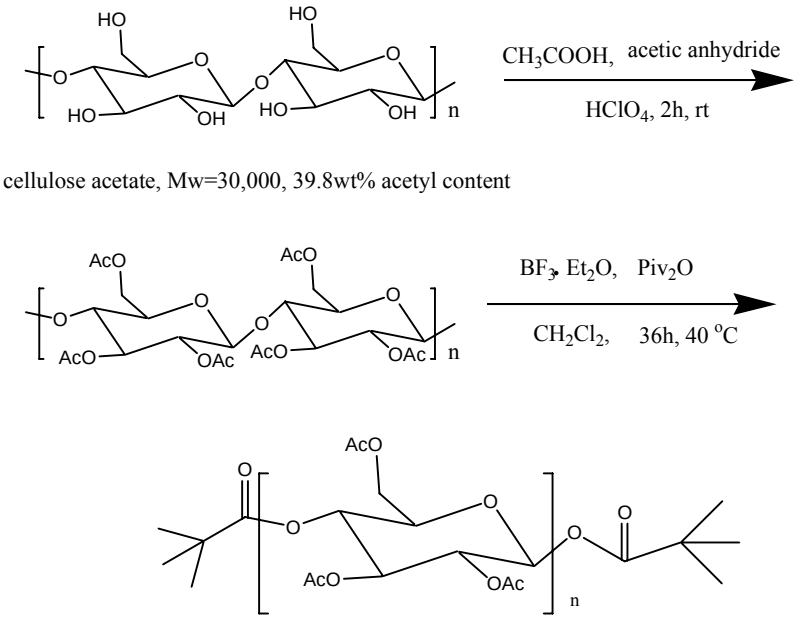
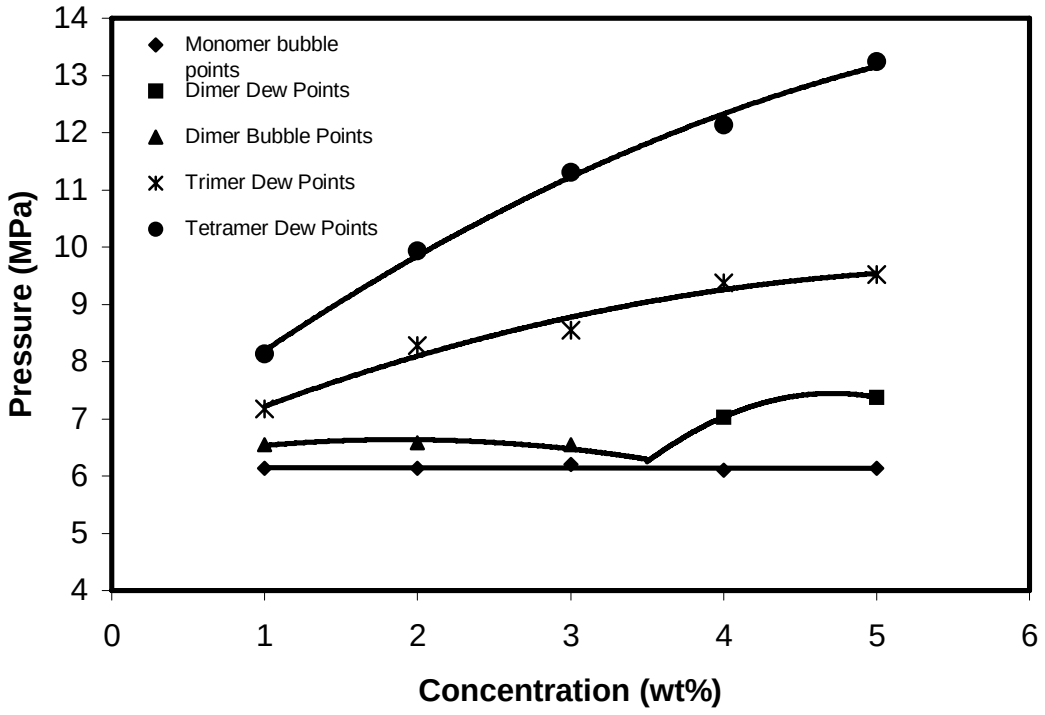


Figure 7: -Pivaloylysis of cellulose triacetate

A pressure-composition phase diagram of CTA oligomers, monomer, dimer, trimer, and tetramers of the oligomer shown in figure 7, is presented in Figure 8. Only bubble points were observed for monomer + CO_2 system within 1-5 wt%. For dimer + CO2 system, dew points were observed for 5 and 4 wt % and bubble point was observed from 3 to 1 wt %. For trimer and tetramer only dew point was observed.



Conclusions

Currently, the three oxygenated hydrocarbon-based polymers that exhibit the greatest solubility in CO_2 include PVAc, poly(AcGIcVE) and amorphous PLA. The pressures required for dissolution, however, are quite high, ranging from 35 – 150 MPa. Small compounds that are rich in acetate groups, including a hydrogen bonding compound, a dendrimer and oligomeric cellulose triacetate, have also been shown to be remarkably CO_2-soluble.

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