

New CO₂ Solvents based on CO₂-philic Oligomers

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ABSTRACT

Several polymers that are soluble in dilute concentration in high pressure liquid or supercritical CO₂ appear to be excellent solvents for the capture of CO₂ from a gas stream. For example, our preliminary results appear to demonstrate the polydimethylsiloxane (PDMS) and polypropyleneglycol dimethylether (PPGDME) absorb slightly more CO₂ at a specified temperature and pressure than polyethyleneglycol dimethylether (PEGDME), the solvent employed in the Selexol process. Perfluoropolyethers (PFPE) also absorb CO₂, but much higher pressures are required to absorb the same amount of CO₂ (on a wt% basis) in PFPE than in PEGDME, PPGDME or PDMS.

INTRODUCTION

CO₂ is commonly removed from gas mixtures by absorption processes. If the gas mixture is at low pressure (e.g. post combustion gas mixtures), chemical absorption employing aqueous amine solutions (i.e. amine scrubbing) is typically used because the reactions that bind CO₂ will occur at low CO₂ partial pressure. For example, mixtures of 30wt% monoethanolamine, MEA, in water reversibly bind CO₂ as two amine groups react with a single CO₂ to form a carbamate. Solvent regeneration is achieved by temperature swing absorption as heating to moderate temperature causes the carbamates to dissociate.

If the gas mixture is at high pressure (e.g. pre-combustion gas mixtures), however, physical absorption is used to remove the CO₂ because the high partial pressure of CO₂ is sufficient to attain high loadings in the solvent. Polyethyleneglycol dimethyl ethers are particularly well suited for absorbing CO₂ [1]. The Selexol® process, for example, is a commercial technology that uses polyethyleneglycol dimethylethers, PPGDME, as the CO₂ (and H₂S) solvent. The rich

solvent is then regenerated at low pressure and high temperature conditions where the CO₂ solubility in the gas decreases substantially.

PEGDME is widely used as a CO₂ physical solvent in the chemical and petroleum engineering industries. When employed in the Selexol process, the solvent is a mixture of PEGDME oligomers with 3 – 9 PEG repeat units, enabling the solvent to have vapor pressure and viscosity values low enough to inhibit evaporative losses and facilitate pumping, respectively. The oligomers are terminated with methyl ether groups, rather than hydroxyls, because the hydroxyl groups are CO₂-phobic moieties that reduce the solubility of CO₂ in a solvent while the oxygen of the methyl ether group promotes solubility by providing an additional site for Lewis acid:Lewis base interactions with CO₂. Methanol has also been used commercially as a solvent for CO₂, but the gas mixture must be chilled to prevent excessive evaporative losses of the alcohol.

The objective of this study is two-fold. First, we assess the viability of several other solvents for CO₂ physical absorption. The choice of solvents has been limited to oligomers that have already been established as “CO₂-philic” by their ability to completely dissolve in CO₂ in dilute concentration at elevated pressure. In other words, these liquid oligomers exhibit low two-phase pressure boundaries with CO₂ on the CO₂-rich compositional end of the pressure-composition (Px) diagram. These candidates include PEGDME, representative of the solvent used in the Selexol process, and three other oligomers known to be more soluble in CO₂ than PEGDME, polypropyleneglycol dimethylether (PPGDME), polydimethylsiloxane (PDMS) and a perfluoropolyether (PFPE). The bubble point locus of these CO₂-oligomer systems is determined over the entire range of compositions at 25 °C. The bubble point values at the oligomer-rich end of the Px diagram will be used to assess the capacity of the solvent to absorb CO₂, and to derive Henry’s law coefficients for each solvent.

EXPERIMENTAL

Materials

PEGDME (M_n = 250, n = 4.64) was purchased from Sigma Aldrich and used as received. PPGDME (M_n = 230, n = 3.2) was purchased from Polymer Source Inc. and used as received. A PDMS (M_n = 237, n = 2) sample was obtained from Dow Corning and used as received. Krytox ® GPL 100 PFPE (M_n = 960, n = 7.1) was purchased from Miller-Stephenson and used as received. The structure of these oligomers is illustrated in Figure 1. CO₂ was purchased from Penn Oxygen and Supply Comp. with a purity of 99.99% and used without further purification.

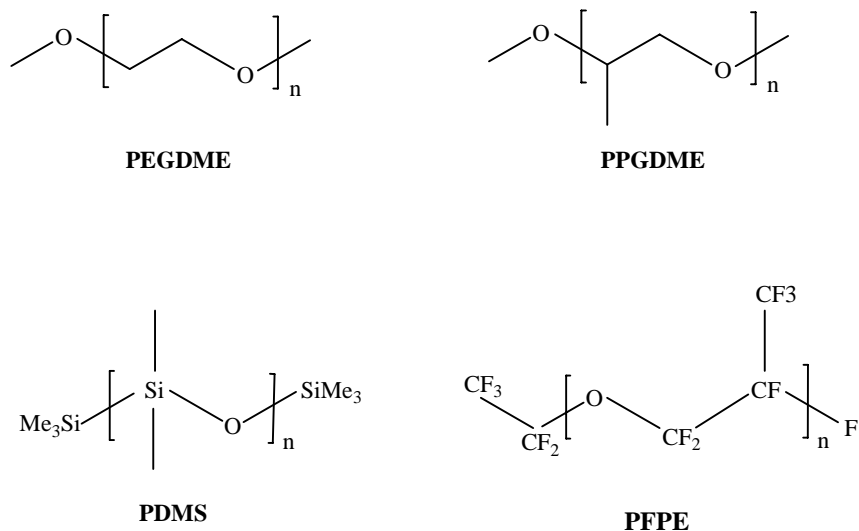


Figure 1. Schematics of the four CO₂-philic polymer

Experimental procedures

Phase equilibrium measurements between the CO₂-philic polymer and CO₂ were carried out in a high pressure, windowed, agitated, variable volume view cell (Schlumberger) using standard non-sampling techniques. The heart of this cell is a thick-walled hollow quartz tube (1.25 in. ID, 1.75" OD) which houses a "floating" piston. An O-ring that encircles the piston separates the cylindrical sample volume above the piston from the overburden fluid below the piston. The quartz tube is retained within a high pressure stainless steel vessel (180 °C 10000 psia) with 1 ½" thick windows on opposing sides. The overburden fluid resides below the floating piston on the inside of the hollow tube, and also in the gap between the cell windows and the outer surface of the quartz, thereby eliminating any pressure drop across the wall of the hollow tube. The entire high pressure cell is enclosed in a temperature controlled air bath capable of controlling the temperature between -20 °C and 180 °C. In a typical experiment, the oligomer sample is first loaded by weight from a syringe onto the surface of the floating piston within the quartz tube. The quartz cell, floating piston and oligomer assembly is then inserted into the high pressure windowed cell and sealed with a cap that houses a magnetic mixer and the port through which gas can enter the sample volume. The piston is then displaced to a position near the top of the cell, thereby minimizing the sample volume and displacing air from the sample volume. The sample volume is then flushed several times with CO₂ (2 psig) in order to assure there is no air present during the experiment. A small amount of high pressure CO₂ then flows into the sample volume from a high pressure positive displacement (PD) pump that retained liquid CO₂ at ambient temperature (~23 °C) and a specified pressure (e.g. 2000 psia) and volume (100 cc). The mass of CO₂ that entered the sample volume is determined by calculating the amount of CO₂ that left the PD pump; a NIST correlation equation is used to determine the CO₂ density in these calculations. Other mixture compositions are attained via the additions of CO₂ to the sample volume. First, the polymer-CO₂ mixture in the sample volume is compressed to the same pressure as the CO₂ in the PD pump. The valve separating the CO₂ and the sample volume is then opened, and liquid CO₂ is displaced into the sample volume at the exact same volumetric flow rate that the sample volume is expanded. This is achieved by advancing the CO₂ PD pump

at the same rate as the overburden fluid PD pump is withdrawn. This results in a well controlled, isothermal and essentially isobaric addition of a specified volume (and thereby mass) of CO₂ into the sample volume.

A mixture of known overall concentration is then isolated from the CO₂ source by closing the valve leading to the CO₂ PD pump, and compressing the mixture, via the addition of the overburden fluid and reduction of the sample volume, until a single phase is attained as the mixture is stirred. The mixer is turned off and the system is very slowly depressurized and expanded by withdrawing the overburden fluid from the cell. Once the bubble point is reached a bubble escapes from the solution and the pressure is recorded. The vapor-liquid line for each polymer-CO₂ pseudo-binary system has been constructed to define the phase diagram at a fixed temperature of 25 °C.

RESULTS AND DISCUSSION

The bubble point loci for the PEGDME-CO₂, PPGDME-CO₂, PFPE-CO₂ and PDMS-CO₂ pseudo-binary systems are reported over the entire range of compositions, Figure 2. Because these results correspond to a temperature of 25 °C, which is slightly below critical temperature of CO₂ (31.1 °C), the bubble point curves are bound by the vapor pressure of CO₂ and by the vapor pressure of the oligomer (which was assumed to be ~0 for the purposes of the data presentation). The Henry's law constants at dilute CO₂ concentration for each respective CO₂-phile are reported as well in Table 1.

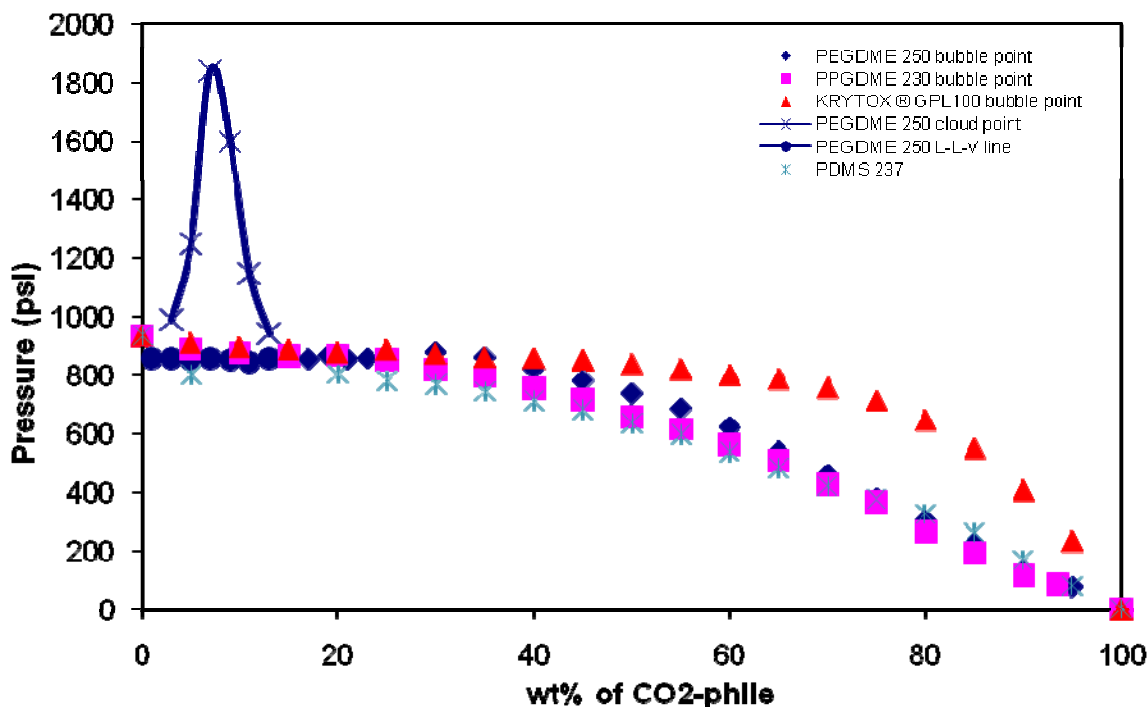


Figure 2. Solubility of CO₂ in each of the four CO₂-philic solvents. T = 25°C.

Three of these solvents exhibit bubble point data across the entire range of compositions with the (possible) exception of PEGDME, which appears to exhibit a small LL region at dilute concentrations of PEGDME in CO₂. (The results of a re-examination of this phase behaviour will be presented at the conference).

The right-hand side, or solvent-rich end, of this diagram is of particular interest for the CO₂ absorption process. Similar results were obtained for the PDMS, PEGDME and PPGDME, while much higher pressure was required to dissolve CO₂ in PFPE (on a wt% basis).

Between 80-100% solvent (20-0wt% absorbed CO₂) it appears that PPGDME is a slightly better solvent than PEGDME, which is slightly better than PDMS. This is also reflected by the Henry's law constants below derived from the data for solutions containing dilute concentrations of CO₂.

CO ₂ -phile	Henry's law constant (psi)
PPGDME	303
PEGDME	335
PDMS	359
PFPE	434

Table 1. Henry's law constants for presented CO₂-philic liquid solvents at 25 °C.

CONCLUSIONS

The solubility of CO₂ has been presented for four CO₂-philes. They were chosen based on their ability to dissolve in CO₂ at low concentration. The pressure required to dissolve CO₂ in PFPE was notably greater than that required for PDMS, PEGDME and PPGDME. Both PEGDME and PDMS appear to have the ability to absorb CO₂ to the same extent as PEGDME. PEGDME, in particular, has a lower Henry's constant than PEGDME, the solvent employed in the Selexol process. Therefore both PPGDME and PDMS will be further investigated over a broad range of molecular weight and temperature.

ACKNOWLEDGEMENT

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REFERENCE

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