Hydrophobic Polymeric Solvents for the Selective Absorption of CO_2 from Warm Gas Streams that also Contain H_2 and H_2O

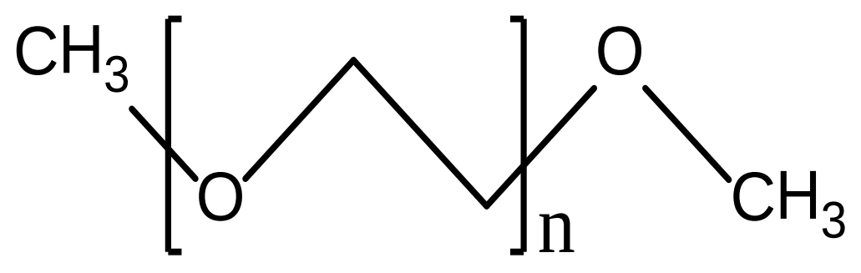
Robert M. Enick, NETL RUA and University of Pittsburgh, USA, Peter Koronaios, NETL RUA Post-Doc, University of Pittsburgh, USA, David R. Luebke, US DOE NETL, USA, Hunaid Nulwala, NETL RUA, Carnegie Mellon University, USA Samantha Warman, University of Pittsburgh, USA, Craig Stevenson, University of Pittsburgh, USA

The post-WGSR fuel gas in an IGCC power plant is at ~250ºC and 800psi (5.5MPa), with a compositions of 31 mol% CO_2, 43% H_2, 23% H_2O, and 3% of other gases such CO, COS, H_2S. The CO_2 partial pressure is about 250psi (1.7MPa). The dew point of the gas mixture is ~180°C. The conventional strategy for the removal of CO_2 from this stream is to cool the it to ~40ºC; the water will begin to condense out of the stream at 180ºC and the vast majority of the water will be removed as a liquid from this stream when cooled to 40ºC. A very hydrophilic solvent, such as the Selexol solvent, which is rich in polyethyleneglycol dimethylether (PEGDME) can then be used to remove the CO_2 from the hydrogen. The hydrogen can then be diluted with N_2 from the air separation prior to combustion.

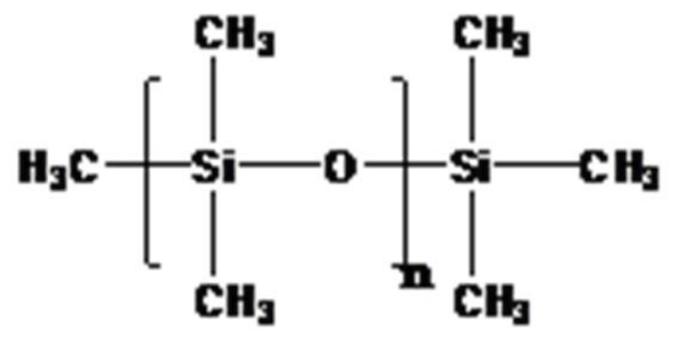
This study considers an alternate means of removing the CO_2 from the post WGSR stream. Rather than cooling the stream and condensing the water prior to absorption of CO_2, the CO_2 is absorbed from the hot or warm, humid stream with a CO_2-selective hydrophobic solvent that absorbs little H_2 or H_2O vapor. In this case the H_2O would dilute the H_2 sent to combustion. Process modeling at NETL indicates that this minimization of fuel gas cooling and heat exchange equipment could increase the thermal efficiency of an IGCC by 1-3 % points.

Solvents such as Selexol that are rich in PEGDME cannot be used for such a process because PEGDME is completely miscible with water in all proportions and would therefore absorb both water vapor and CO_2. Out team is using PEGDME as a "control" and assessing the viability of the five hydrophobic solvents for this high temperature absorption process:

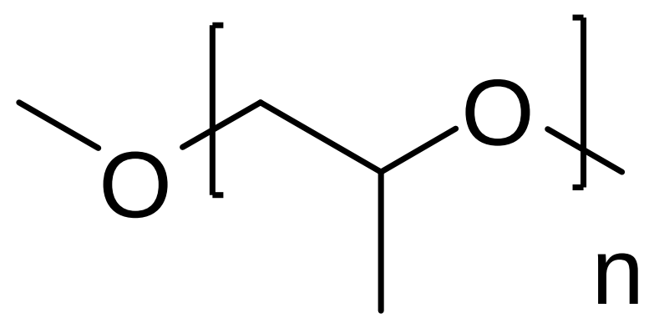
Polyethyleneglycol dimethylether (PEGDME 250)
Extremely hydrophilic



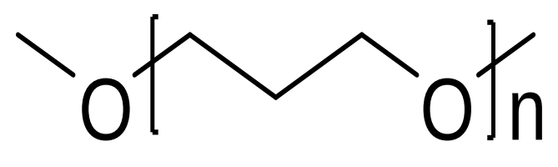
Polydimethylsiloxane (PDMS 550)
Extremely hydrophobic, high thermal stability



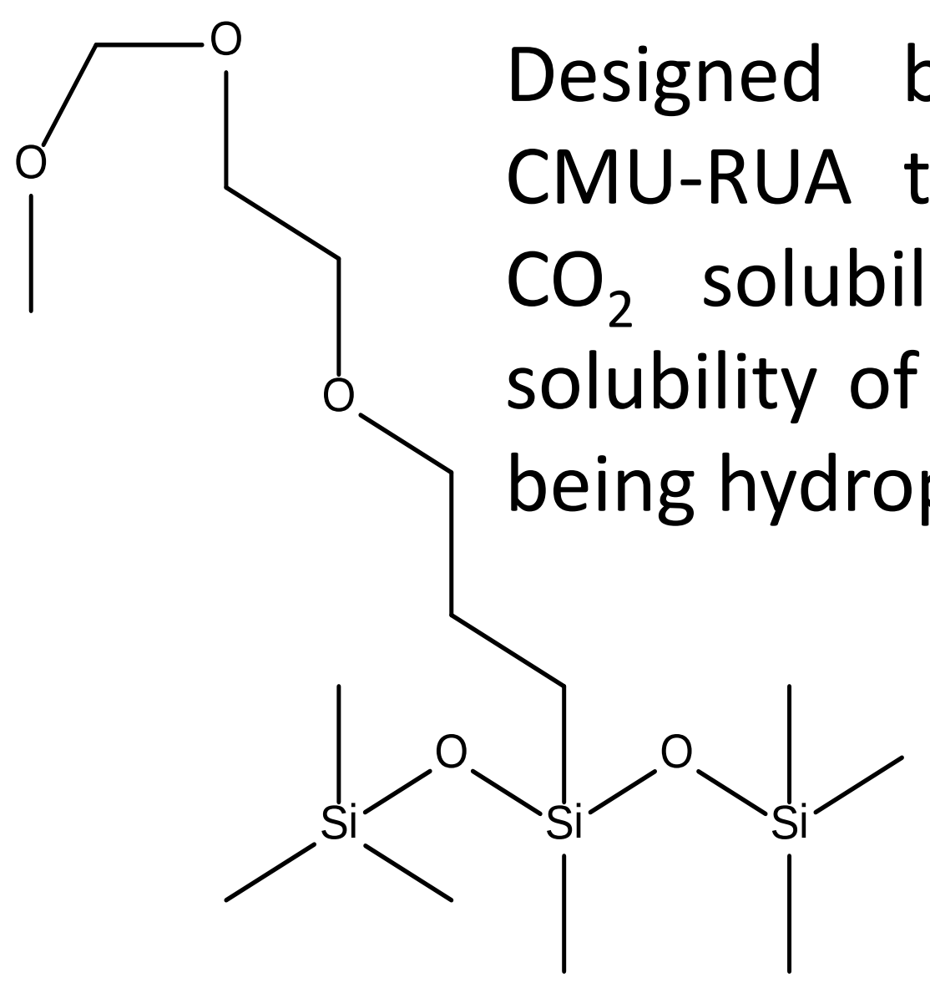
Polypolypropylene dimethylether PPGDME-B 430
PPGDME absorbs ~2wt% water at 25ºC, but slowly



PPGDME-L 650
forms rigid gels upon exposure to liquid water

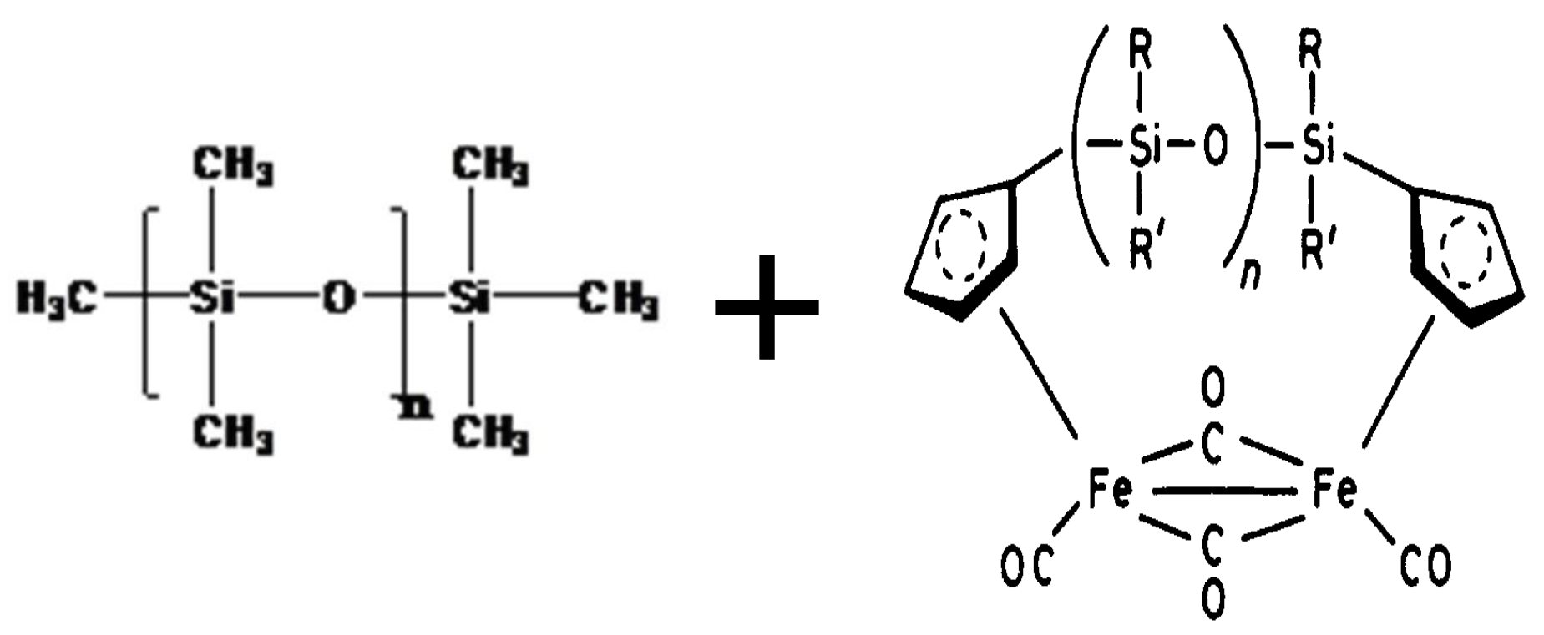


Hybrid PDMS-PEGDME
(2,2,4-trimethyl-4-((trimethylsilyl)oxy)-3,8,11,14-tetraoxa-2,4-disilapentadecane)

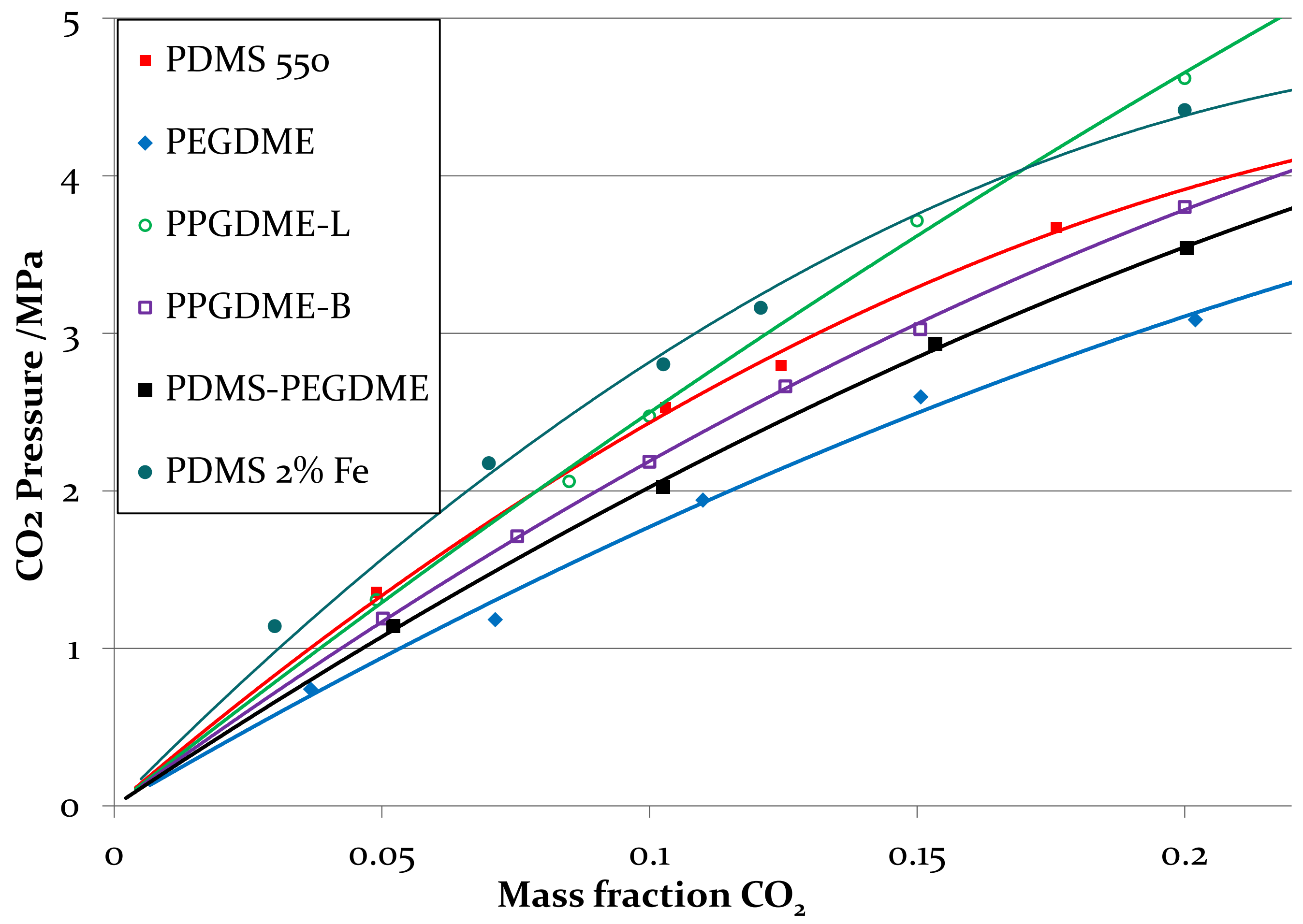


Designed by Nulwala of CMU-RUA to provide high CO_2 solubility of low H_2 solubility of PEGDME, while being hydrophobic

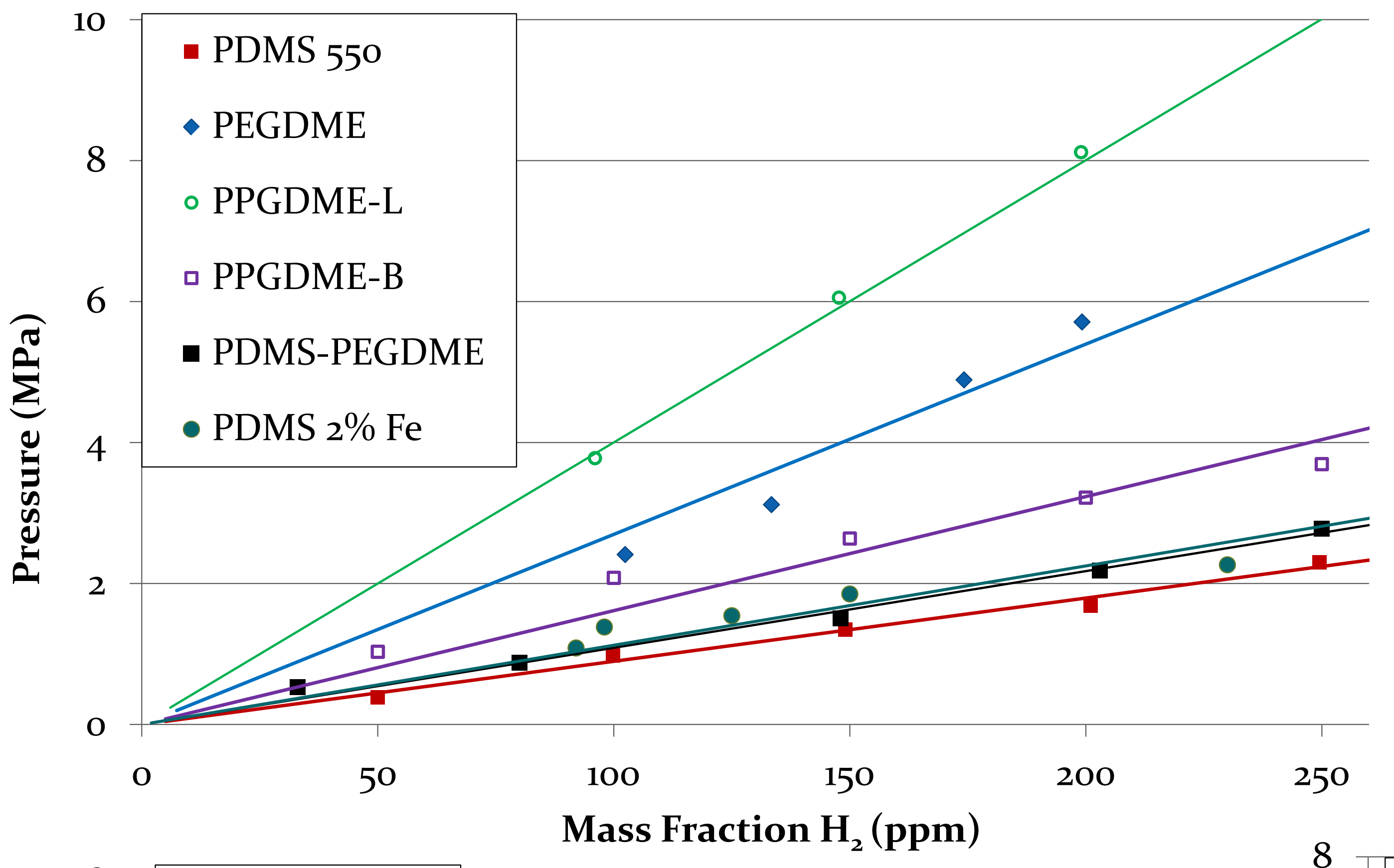
PDMS 6000 + 2% Fe-siloxane high temperature stabilizer
Even higher thermal stability than PDMS



Possible structure: M.Moran, I.Cuadrado, J.R.Masaguer, J.Losada, J.Chem.Soc.Dalt.Trans., 18(1988) 833-8

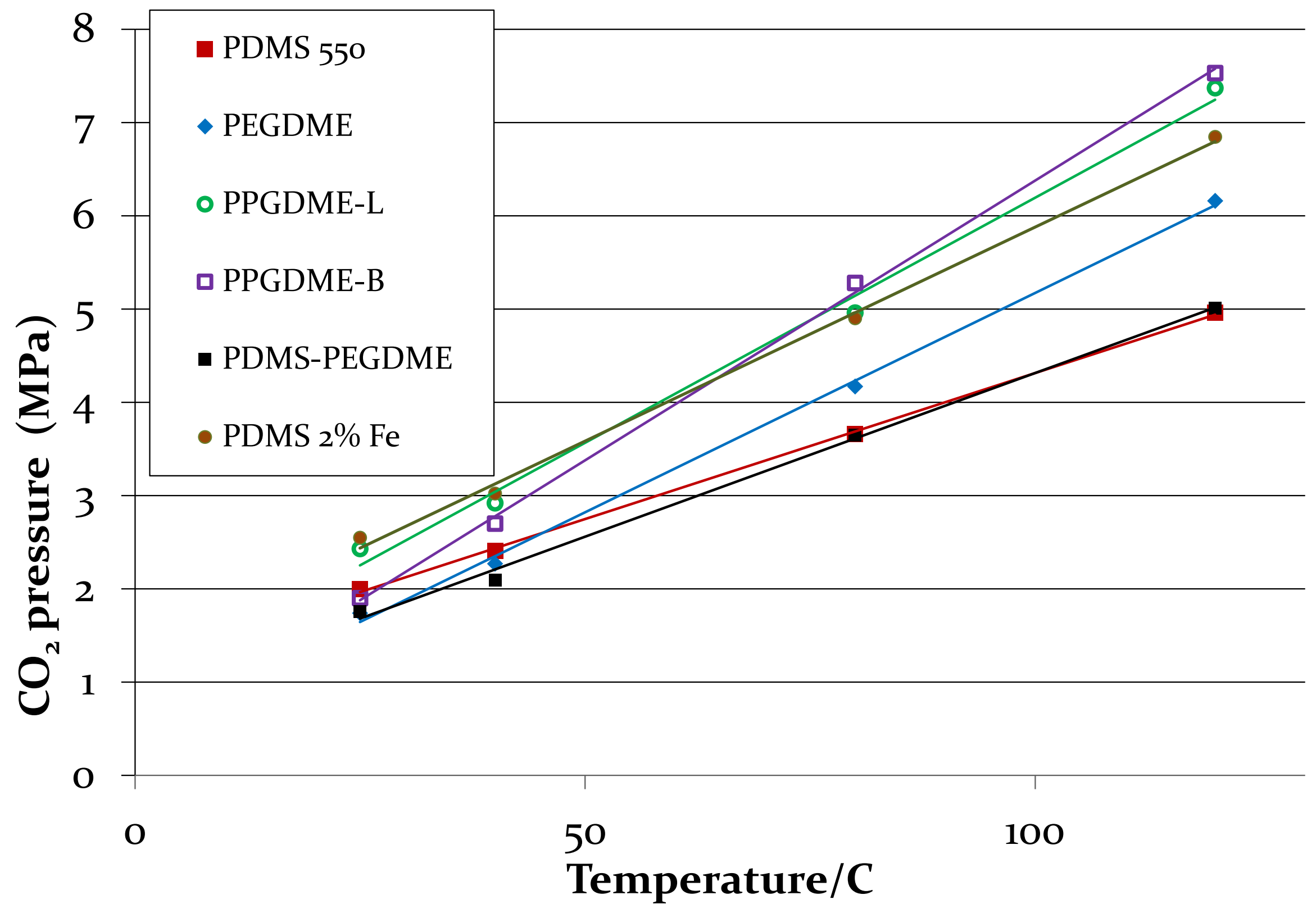


CO_2-solvent bubble point pressure at 25C. The lower bubble point curves correspond to the strongest CO_2 solvents (desirable). The solvents are all reasonable CO_2 solvents. PEGDME is the best CO_2 solvent. The PDMS 6000 + Fe solvent is the weakest of the CO_2 solvents primarily due to it high MW.

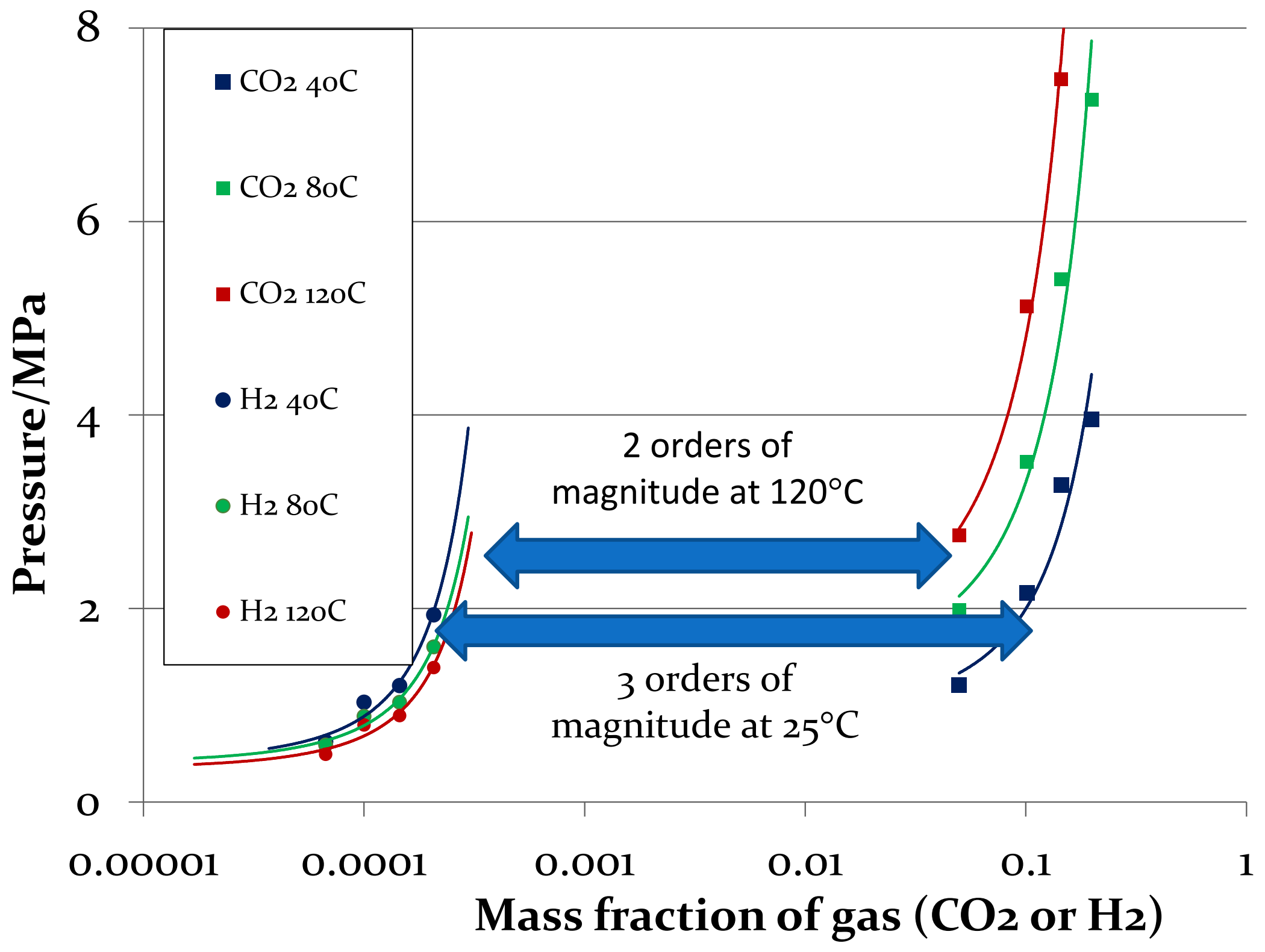


H_2-solvent bubble point pressure at 25ºC. The higher bubble point curves correspond to the weakest H_2 solvent (desirable). PPGDME-L is the weakest H_2 solvent, PDMS 550 is the strongest H_2 solvent. In general H_2 exhibits its lowest solubility in linear (monomer) polymers due to smaller free volume.

H_2 solubility increases with increasing temperature (not shown in this plot to the left, but shown below) due to increased free volume of polymers at elevated T.



The CO_2 solvent strength for all solvents decreases with increasing temperature, as shown in this plot of the bubble point pressure at 10wt% CO_2 as a function of T for each solvent. This is due to diminished strength of thermodynamically favorable CO_2-monomer Lewis acid:Lewis base interactions at elevated T.



Solubility of CO_2 and H_2 in PDMS-PEGDME hybrid at various temperatures. Because CO_2 solubility decreases and H_2 solubility increases with T, the separation will be more difficult at higher T values. This occurs for all solvents.