CO_2 capture using CO_2-philic polymers as hydrophobic liquid solvents or crosslinked polymeric membranes

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Objective 1: Use **polymeric membranes** to separate CO_2 from mixed gases; CO_2/CH_4(natural gas treatment), CO_2/H_2(pre-combustion gasification+water-gas shift), CO_2/N_2(post-combustion separation). This membrane study focuses on **CO_2/H_2** separation results. Ultimately it is desired to remove only CO_2 (not water) from the $CO_2/H_2/H_2O$ gas mixture.

Objective 2: Use **liquid polymers or oligomers as solvents** to separate CO_2 from high pressure mixtures, such as the $CO_2/H_2/H_2O$ gas mixture in an IGCC plant. This report details the solubility of CO2 and water in the solvents. Ultimately it is desired to remove only CO_2 (not water) from the $CO_2/H_2/H_2O$ gas mixture.

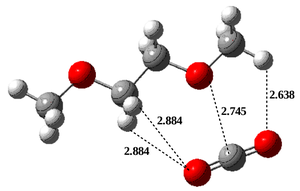
Our unique approach: To design membranes and solvents that are superior to the state-of-the-art products by using novel, **highly CO_2-philic polymeric** materials. We hope to design solvents that are superior to commercial solvents based on PEG, and commercial crosslinked membranes based on PEG.

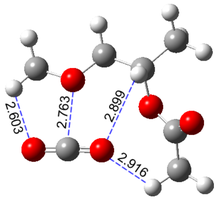
What makes a polymer or oligomer highly CO_2-philic?

"CO_2-philic" oligomers and polymers

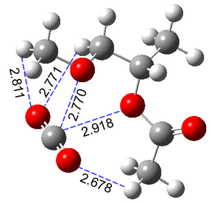
Key Characteristics

Multiple sites (typically O and H atoms) for Lewis acid:Lewis base or weak hydrogen bonding interactions with CO_2, CO_2-PEG example shown below





CO_2-PAO interactions shown above and below



The polymers and oligomers typically have low Tg values and most are liquid at ambient temperature

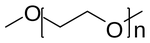
The polymers that are solid at room temperature (e.g. PFA,) are amorphous with melting points slightly above ambient temperature

The polymers and oligomers do not contain CO_2-phobic groups, such as hydroxyl groups and long linear alkyl chains

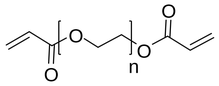
Polymers and oligomers can actually dissolve at concentrations of several wt% in dense CO_2 at extremely high pressures (7-70 MPa)

CO_2-philic Polymers & Oligomers PEGDME, PEGDA, PDMS, PPGDME, PPGDA, PBGDAc, PBGDA, PFPE, PHDFA, PAO, GTA

PEG: The state-of-the-art fluid for CO_2 solvents and CO_2 selective membranes

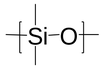


Poly(ethylene glycol) dimethyl ether **PEGDME** S, SLM
A major constituent of Selexol solvent and of crosslinked commercial CO_2-selective membranes



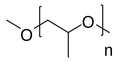
Poly(ethylene glycol) diacrylate XLM – A commercial CO_2-selective membrane is based on **crosslinkable PEG**

Can we do better than PEG as a solvent and a membrane?

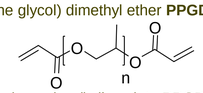


Poly(dimethylsiloxane) **PDMS** – S, SLM
Commercially available as liquid or as a XLM crosslinked membrane

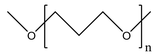
S = liquid solvent
SLM = supported liquid membrane
XLM = crosslinked membrane
CM = cast membrane
(b) = branched monomer
(l) = linear monomer



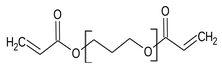
Poly(propylene glycol) dimethyl ether **PPGDME(b)**, S, SLM



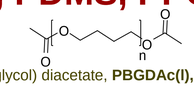
Poly(propylene glycol) diacrylate **PPGDA(b)**, XLM



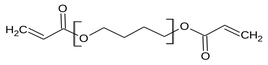
Poly(propylene glycol) dimethyl ether **PPGDME(l)**, S, SLM



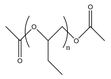
Poly(propylene glycol) diacrylate **PPGDA(l)**, XLM



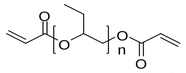
Poly(butylene glycol) diacetate, **PBGDAc(l), (PTMEGDAc)** S, SLM



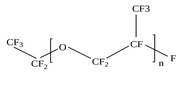
Poly(butylene glycol) diacrylate **PGBDA(l)** XLM



Poly(butylene glycol) diacetate **PBGDAc(b)** S, SLM

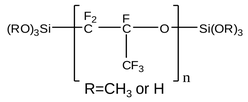


Poly(butylene glycol) diacrylate **PBGDA(b)** XLM

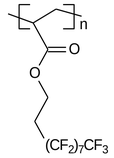


PFPE

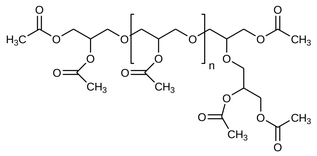
Perfluoropolyether **PFPE** S, SLM



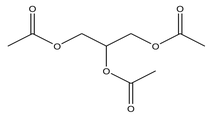
Perfluoropolyether **PFPE** XLM



poly(heptadecafluorodecylacrylate) **PFA** CM

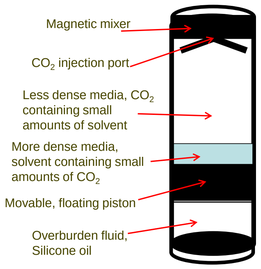


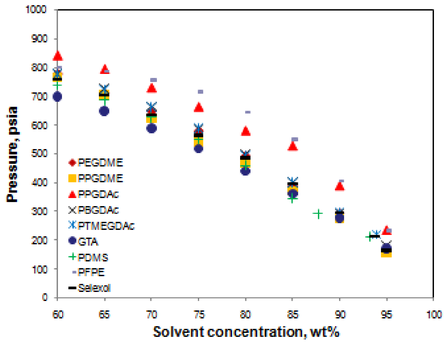
Poly(acetoxy oxetane) **PAO** S, SLM



glycerol triaceate **GTA** S, SLM

Liquid Solvent Solubility





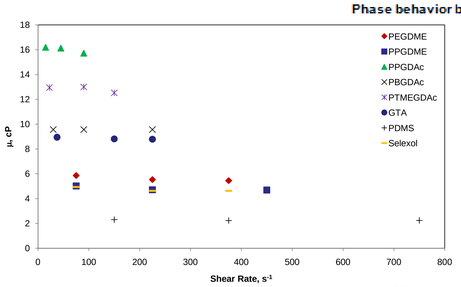
Phase behavior bubble point loci for all solvents tested at 25ºC

Henry's law constants for all solvents at 25.0 and 40.0ºC

Solvent	Henry's Law constant KH (psi)	
	25.0 ºC	40.0 ºC
SelexolTM	2636	3296
PEGDME	2593	3180
PPGDME	2469	3267
PPGDAc	3524	3938
PTMEGDAc	2682	3342
PBGDAc	2669	3131
PDMS	2408	3515
GTA	2303	2838

Water miscibility at ambient pressure

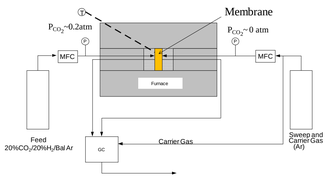
Solvent	Miscibility (g H_2O/g solvent)	
	22 ºC	40 ºC
SELEXOL™	Fully miscible	Fully miscible
PEGDME	Fully miscible	Fully miscible
PPGDME	0.021	0.028
PPGDAc	0.022	0.025
PTMEGDAc	0.017	0.024
PBGDAc	0.018	0.031
PDMS	Immiscible	Immiscible
GTA	0.046	0.062



Viscosity of oligomers at potential operating conditions, 40ºC.

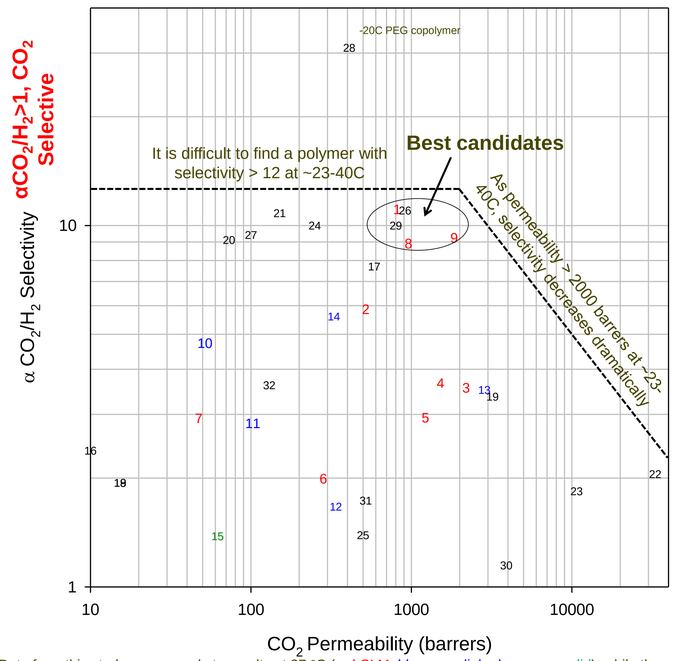
Liquid Solvent Solubility Conclusions: PPGDME, PBGDAc, and PDMS were the most promising materials tested. Each of these solvents expressed comparable CO_2 solubility results with PEGDME. PDMS exhibited the lowest viscosity of any oligomers tested followed by PPGDME then PEGDME. PDMS also exhibited the lowest miscibility with H_2O followed by both forms of PBGDAc followed by PPGDME while PEGDME is fully miscible with H_2O. **Liquid solvents composed of PDMS, PPGDME, or PBGDAc may be promising, particularly when NOT absorbing H_2O is a priority. GTA gave promising solubility and viscosity results but would be extremely difficult to produce economically.**

Membrane Results



$$P_a = \frac{n_a t_m}{\Delta p_a}$$

Our study quantified mixed gas permeance results, rather than the simpler but significantly less accurate technique of comparing pure gas results



Data from this study corresponds to results at 37 ºC (red-SLM, blue-crosslinked, green – solid), while the literature results (black) for CO_2/H_2 separation factor versus CO_2 permeability at temperatures of 23 – 40 ºC

1	PEGDME
2	PPGDME
3	PDMS (5 cSt)
4	PDMS (100 cSt)
5	PFPE (GPL 100)
6	PFPE (GPL 107)
7	PAO
8	PBGDAc
9	GTA
10	PEGDA (XLink)
11	PPGDA (Xlink)
12	PFPE(Xlink)
13	PDMS(XLink)
14	PBGDA(XLink)
15	PFA
16	PTFE
17	Polyurea-Polyether
18	Poly(styrene-co-butadiene)
19	Poly(dimethyl siloxane)(PDMS)
20	PEBAX
21	PEBAX/PEG50
22	Polytrimethylsilylpropyne
23	Poly(4-methyl-2-pentyne)
24	Polyphosphazene
25	Poly(tert-butylacetylene)
26	Poly(ethylene glycol) diacrylate
27	Crosslinked PEG copolymer
28	Crosslinked PEG copolymer (T=-20C)
29	Ionic Liquid [hmim][Tf2N]
30	TFE/BDD87
31	PFOA
32	PFOMA

Membrane Conclusions: PEG, PBG(l), and GTA SLM were the most promising materials. Our XLM of PBG(l) were superior to our XLM of PEG. PPG(l) is currently being tested. **Crosslinked or supported membranes composed of linear monomers of PPG and PBG may be promising. GTA gave promising SLM results but would be extremely difficult to produce economically or to crosslink,**

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