Effect of Molecular Structure on the CO_2 Separation Properties of Hydrophobic Solvents Consisting of Grafted Poly Ethylene Glycol and Poly Dimethyl Siloxane Units

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Abstract

This work describes the preparation of a set of nine new novel hydrophobic PEG-substituted solvents. These solvents include linear, T-shaped, and disubstituted conformations of the PEG grafted with PDMS molecule. The effect of changing both the molecular conformation and length of PEG side-arm on the physical properties and CO_2 absorption capacity was studied. These solvents are intended for separation of CO_2 and H_2 in pre-combustion CO_2 capture and are intended to replace the current-state-of-the-art glycol-based solvents and operate at a higher temperature. The properties of the disubstituted solvents are exceptionally well suited for pre-combustion CO_2 capture applications because of their hydrophobicity, high CO_2 solubility, low evaporation rate, and lack of foaming.

Introduction

The removal of acid gases and greenhouse gases from industrial fuel sources will continue to be a growing world-wide market.[1] H_2S and CO_2 removal from industrial fuel streams is crucial for the development of chemical processes that convert coal, biomass, and carbon-containing waste streams into H_2, ammonia, electricity, and/or hydrocarbon fuels. A variety of methods have been proposed to capture CO_2 from H_2-rich fuel streams including solvent, sorbent, and membrane technology. At commercial scale, this pre-combustion capture of CO_2 is typically accomplished with physical solvents, given that the high partial pressure of CO_2 in the syngas gas stream is sufficient to dissolve significant amounts of CO_2 into the solvent without the need for chemical binding.[2] Physical solvents are favored over chemical solvents in systems where the partial pressure of CO_2 is high (> 5 bar), as they can be easily regenerated via pressure swing.[3-5] At the outlet of the water gas shift (WGS) reactor, the typical pre-combustion fuel gas stream for a coal gasification system consists of 30-32 mol% CO_2, 43 mol% H_2, 23 mol% H_2O, and 3 mol% of impurities such as CO, COS, and H_2S, at a temperature of around 250℃ and pressure of around 5 MPa.[6]

The current state-of-the-art of CO_2 capture technologies for pre-combustion processes, such as in Integrated Gasification Combined Cycle (IGCC) systems for electric power generation,[7] employ the glycol-based Selexol™ solvent that preferentially absorbs CO_2 and sulfur compounds from the syngas mixture.[8] Other commercially-available physical solvents include methanol

(Rectisol®),[9] N-methyl-2-pyrollidone (Purisol®), and propylene carbonate (Fluor Solvent™). The hydrophilic nature of Selexol means that the syngas must be cooled to quite low temperatures (10°C - 40°C) to remove water vapor in the syngas. The presence of water in Selexol will increase the viscosity of the solvent and will decrease the CO_2 uptake, which is why as much water as possible is condensed from the syngas before contacting Selexol. Therefore, one major area for improvement in the baseline IGCC process is reducing the energy penalty associated with cooling the syngas to below room-temperature to remove CO_2, H_2O and H_2S prior to combustion.[6] It has been reported that the electrical efficiency of an IGCC power plant could improve by 3 basis points, and the levelized cost of electricity with carbon capture could decrease by 20% when implementing warm gas clean-up of both pollutants and CO_2.[10]

While hydrophilicity is an ideal quality for a solvent in the natural gas industry, it is not ideal for IGCC applications. For natural gas transportation, there are strict limitations of the amount of water vapor permitted in natural gas entering a pipeline. So, a solvent with a high affinity for water is important for dehumidifying the acid-gas-free natural gas, whereas for many other industrial syngas applications, water vapor does not need to be removed from the clean H_2-rich stream. For example, in IGCC applications, a certain amount of inert diluents (N_2, H_2O) can be desirable in the H_2 fuel gas stream being sent for combustion in the gas turbine. The ideal qualities of a physical solvent for IGCC applications are high CO_2 uptake, extremely high H_2S uptake, low uptake of $H_2/CO/N_2/CH_4$, high CO_2 diffusivity, low vapor pressure, low tendency to foam/aerosolize, high mass density, low water uptake, and most importantly chemical stability above ambient temperature. Bara et al. reported that the inclusion of etheric side chains in the form of poly(ethylene glycol) (PEG) units of varying lengths can impart favorable gas absorption selectivity for CO_2 over CH_4 and N_2 in imidazolium ionic liquids while maintaining good CO_2 solubilities and other physical properties.[11-13]

We also reported on the use of this approach previously as being successful for a linear conformation of PEG grafted to poly(dimethyl siloxane) (PDMS) that is selective for CO_2 over H_2 (this solvent was named PEG-Siloxane-1 in the corresponding reference).[14] However, this linear PEG-PDMS hybrid solvent had some drawbacks including an only moderate selectivity for CO_2/H_2 and severe foaming when exposed to flowing gas. Foaming is of concern as it can reduce the performance of the absorption column by increasing the pressure drop, reducing the mass transfer and lowering overall column capacity, which can lead to operational difficulties and increased process cost.[14]

This work describes the preparation of nine new hydrophobic PEG-substituted solvents of similar construction to PEG-Siloxane-1. These solvents include linear, T-shaped, and disubstituted conformations of PEG grafted with PDMS. The effect of changing both the molecular conformation and length of PEG side-arm on the physical properties and CO_2 absorption capacity was studied. In general, the performance of linear and T-shaped molecules was similar, including the tendency to foam. However, the disubstituted PEG-PDMS molecule stood apart as being non-foaming, and having improved thermal stability, reduced volatility, and lower fractional free volume (FFV) for improved CO_2/H_2 selectivity. This particular solvent conformation embodies all the most desirable properties for a solvent that is tailored to pre-combustion CO_2 capture, making it a strong candidate to outperform glycol-based solvents for our target application.

Experimental

Syntheses

The preparation of all the solvents discussed in this work were accomplished by way of a hydrosilation reaction between commercially-available polyethylene glycol olefins and siloxysilanes, catalyzed by Pt-type catalyst. The method of preparation of these compounds was derived from reactions reported by Lewis, et al,[15-16] and used at NETL in previously preparing T-4PEG (**5**).[17] The different siloxane and poly(ethylene glycol)-olefin (PEG-olefin) reagents used to prepare the solvents in this work are shown in the supplemental information; all reagents except 1,1,1,3,3,5,5-heptamethyltrisiloxane were used as received from Gelest; 1,1,1,3,3,5,5-heptamethyltrisiloxane was used as received from BOC Sciences. Both disub-3PEG (**7**) and disub-4PEG (**8**) as well as T-4PEG (**5**) were all scaled up to approximately 0.5 L quantities to provide sufficient volumes for foaming tests.

These reagents were combined into nine different products as illustrated in Figure 1, which shows the three different conformations of products prepared: linear, T-shaped, and disubstituted. Linear products were prepared from equimolar mixtures of terminal siloxane and PEG-olefin (linear-*n*PEG); T-shaped products were prepared from equimolar mixtures of internal siloxane and PEG-olefin (T-*n*PEG). Disubstituted products were prepared from the 2:1 mixtures of PEG-olefin and 1,3-disilane (disub-*n*PEG). Three different lengths of PEG-substituted product were prepared for each conformation; all the products prepared and studied in this work are listed in Table 1.

The synthetic schemes used to prepare linear-*n*PEG, T-*n*PEG, and disub-*n*PEG, are shown in the supplemental information, with the preparation of T-4PEG (**5**) having been previously reported.[18] One reference was found which cited the use of T-3PEG (**4**) as an electrolyte additive for rechargeable lithium cells, but no details were provided on how it was synthesized.[19] Full experimental details on the preparation of all nine products are provided in the supplemental information, including characterization data and isolated yields.

Instrumentation

Density measurements were completed on a Rudolph Research Analytical DDM 2911 automatic density meter at 25°C; all samples were measured as five replicates and the average density was reported. Moisture content was determined using a Metrohm Titrando Karl Fisher titration system at 120°C using 50 mL/min N_2 gas flow in oven mode; all samples were measured as three replicates and the average moisture content was reported. Viscosity measurements were performed on a Rheosense model μVisc micro-viscometer outfitted with a temperature controller set to 30°C; all samples were measured as five replicates and the average viscosity was reported.

Thermogravimetric analyses (TGA) were collected on a TA Instruments SDT-Q600 using 50 mL/min air as a sweep gas. FTIR spectra were collected using a Bruker Vertex 70 spectrometer, using neat films of liquid applied to a KBr ATR window. Electrospray ionization (ESI) mass spectra were collected on dilute acetonitrile solutions using an Agilent 6520 QTOF LC-MS in positive ion mode. NMR data were collected on a Bruker Avance III 400 MHz spectrometer using a 5mm BBFO+ probe. All ^{1}H and ^{13}C NMR spectra were referenced to their respective solvents' resonances.

Gas Absorption Experiments

Gravimetric CO_2 adsorption measurements were conducted on a Hiden IGA-001 microbalance. Samples (30-50 mg) were activated by purging with CO_2 at 70 mbar at 40°C until the sample weight stabilized. Isotherms were then measured under flowing CO_2 regulated by a mass flow controller and back pressure regulator. Equilibrium was determined at each pressure step using an internal fitting algorithm in the instrument control software. Buoyancy corrections were then applied to the final equilibrium weights using known densities of all components in the sample and counter weight chambers from gas densities calculated using REFPROP software from NIST. An additional correction (approximately 5% of the adsorbed mass) was also applied to the final equilibrium sample mass at each pressure point to account for the small change in buoyancy force which results from volume expansion of the solvent during CO_2 adsorption.[20-21] The volume expansion of the solvent was estimated from the mole fraction of CO_2 adsorbed using the molar volume of liquid CO_2 at 25°C (density of 0.7105 g/mL, 16.15 mol/L).

Vapor Pressure Experiments

The vapor pressure of the solvents was measured in a 1-L agitated reactor manufactured by Autoclave Engineers, Inc. available at the Reactor and Process Engineering Laboratory at the University of Pittsburgh, for which extensive details regarding the equipment are available elsewhere.[22] Two thermocouples [K-type], one for the liquid and the other for the gas phase, and a Setra pressure transducer with a sensitivity of 12.4 Pa, were used to measure the change of pressure and temperature and transmit the signal to the monitoring and data acquisition system.

The experimental procedure used for determining the vapor pressure of the solvents was as follows: (1) 200-400 mL of a solvent were loaded into the reactor; (2) the reactor was slowly vacuumed for 20 min at room temperature while simultaneously mixing to completely remove any absorbed gases; (3) the system was slowly heated until the desired temperature was reached (typically 85°C), then the heating jacket was shut down and the system was allowed to cool down to room temperature - the pressure and temperature within the reactor was monitored.

Foaming Experiments

Experiments to determine the foaming behavior of the solvents were carried out in a 4-liter Zipper Clave reactor equipped with two Jerguson windows available at the Reactor and Process Engineering Laboratory at the University of Pittsburgh, for which extensive details about this system have been published elsewhere.[22] Between 200 – 400 mL of the solvent were placed in a glass liner within the 4-L ZipperClave reactor, and gas was introduced at a pre-determined flow rate using a 0.25" line extended to the bottom of the glass liner. The foaming behavior of the liquid was then visually reported. Two main foaming parameters were recorded, namely the foam head height, which refers to the length of the foam head above the liquid surface, and the foam stability, which refers to the time taken by the foam to fully decay, after gas flow is stopped.

Computational Details

Ab initio (AI) gas phase calculations were performed to calculate the charges on each atom of the solvents and their interaction with CO_2. For each molecule, the geometry optimization was performed at the B3LYP/6-311++g(d,p) level of theory followed by charge calculations by using the CHELPG protocol.[23] The CO_2-molecule dimer was also optimized at the B3LYP/6-311++g(d,p) level of theory followed by single point energy calculation at the MP2/cc-pVTZ level of theory to obtain CO_2 interaction with each molecule. To account for the basis set superposition error, we have used counterpoise corrections in both geometry optimization, frequency, and single point calculations for dimer computations. More calculation details were described in our previous work.[24-25] All AI calculations were performed by using the Gaussian 09 program.[26] All FFV calculations were calculated by using a modified Bondi method,[27] which has been implemented in an in-house software package at NETL.

The fractional free volume was calculated to be FFV = $(V-V_0)/V$, where V is the molar volume for the compounds at the temperature of interest and V_0 is the occupied molar volume at 0 K, which is given by $V_0 = f \cdot V_{vdw}$, where f was set to be 1.3 in this work.[28-30] The value for V_{vdw} was calculated by using the method developed by Zhao et al.,[27] which has been implemented in our in-house software package at NETL. To validate our FFV calculations, we have recalculated the FFV value for n-hexane by using a molecular weight of 86.178 g/mol and a density of 0.6552 g/cm^3 at 298 K, the FFV was calculated to be 0.331, very close to the value of 0.324 obtained by Lin and Freeman,[31] with a difference of 2%. If the group-contribution method was used, we recalculated the FFV value for n-hexane to be 0.325, nearly identical to the value obtained by Lin and Freeman.[31]

Results and Discussion

Physical Properties

Physical properties for all solvents studied are listed in Table 2, with the table entries arranged according to conformation. The densities of all nine products were approximately 1 g/mL, with the densities of the linear and T-shaped products being slightly lower than for the disubstituted products. The viscosities for all nine products were all less than 16 mPa·s, with the viscosities for the linear and T-shaped products being roughly half that of the disubstituted products. The water content after drying for all molecules was consistently low, despite having been thoroughly water-washed; all moisture contents were measured below 5000 ppm, often being lower than 1000 ppm.

When selecting a physical solvent for CO_2 absorption, it is beneficial to minimize both the solvent's density and viscosity. Lower density results in a larger FFV in the solvent, providing more space for the CO_2 to be accommodated, at least in solvents with similar chemical structures. However, this can also leave more space for other gases, like H_2, which may result in lower CO_2 selectivities, although CO_2 will always absorb at greater amounts than H_2 based on critical properties. For each configuration, as the length of the PEG arm increases, the density increases and the FFV decreases. Lower viscosity improves the diffusion of CO_2 into the solvent, reducing the time required to absorb CO_2; it is also easier to manipulate non-viscous solvents, which keeps equipment costs and pumping power down. As the length of the PEG arm increases, the viscosity also increases.

CO_2 Absorption

All nine solvents prepared in this work were tested for CO_2 absorption at 25 and 40°C, using pure gas CO_2 pressures from 0 to 20 bar by thermogravimetric analysis (TGA). Plots of moles of CO_2 dissolved per liter versus CO_2 pressure are illustrated in Figure 2a (25°C) and 2b (40°C), with the linear fit for the largest slopes shown by a dashed line. The data were corrected for CO_2 volume of expansion at both temperatures. Higher capacity for CO_2 absorption is reflected in larger slopes for the linear fit for these plots. The slope, normalized slope, and correlation coefficient for each solvent at both temperatures are listed in Table 3. These plots are linear ($r^2 \geq 0.994$) and the average absolute percent deviation (AAPD) for these linear fits were all at or below 9%.

As expected, CO_2 was more soluble in the solvents at 25°C, with linear-3PEG (**1**) showing the highest slope at this temperature. At 40°C, CO_2 had the highest solubility in T-3PEG (**4**), with the solubility for all solvents ranging from 66 to 72% of the value at 25°C. The Clausius-Clapeyron equation can use the slopes of the CO_2 absorption isotherms to calculate the enthalpies of absorption for these solvents:

$$\Delta H_{abs} = -R\,(\ln(K_2\,/\,K_1))/(1/T_2 - 1/T_1)$$

where ΔH_{abs} is the CO_2 heat of absorption, R is the gas constant, K_2 and K_1 are the slopes for the absorption isotherms at temperature T_2 and T_1, respectively, and T_1 and T_2 are temperatures (in K) at which the CO_2 absorption isotherms were measured. The ΔH_{abs} values for CO_2 absorption in various solvents studied in this work were found to vary between -17 to -21 kJ/mol. Comparison of the solvents tested was simplified by standardizing the CO_2 absorption slopes at each temperature to that of the maximum slope and expressing the remaining slopes as a fraction of the maximum and averaging the slopes for each conformation and PEG arm length. The differences between solvents at each temperature can then be expressed as a percentage, with the results being listed in Table 4.

At 25°C, the order of CO_2 absorption by conformation is linear > T-shaped > disubstituted. The order is switched to T-shaped > disubstituted > linear at 40°C. The steric complexity of the T-shaped and disubstituted molecules may be prevented from adopting amenable conformations for dissolving CO_2 at lower temperatures, whereas this barrier may be overcome as temperatures increase.

Thermal Properties

All nine versions of solvent were studied by TGA to determine the thermal stability of the various conformations. A small aliquot of each molecule (ca. 10-15 mg) was loaded into an alumina TGA pan and temperature was ramped to 750°C at 10°C/min under 50 mL/min air while the sample mass was recorded. The first derivative maximum (T_{dec}) for each solvent was taken as a measure of the point at which the maximum rate of sample loss was experienced. The results are listed in Table 5, which shows that the decomposition temperature increases with increasing molecular weight for all three conformations. The linear molecules show the lowest T_{dec} values while the disubstituted molecules show the highest T_{dec} values. The thermal stabilities of the T-shaped molecules seem to be nearer those of the disubstituted molecules, even though their molecular weights are identical to the linear analogues.

Selected products were also tested for evaporation by exposing aliquots to 80°C temperatures for a day or longer under 50 mL/min air flow to estimate the amount of weight loss due to volatility. The results are also listed in Table 5, and the results for the three disubstituted analogues show that the weight loss decreases with increasing molecular weight, as shown in Figure 3. A relatively linear weight loss was observed for all three disubstituted molecules after the first 120 min of exposure at 80°C, up to 2000 min. The weight loss results for linear-, T-, and disub-4PEG (**2**, **5**, **8**) also show this trend, with the linear and T-shaped analogues losing mass at a substantially higher rate than the disubstituted analogues under identical conditions. The results also suggest that while the T-shape imparts slightly superior thermal stability, it is slightly more volatile despite having a molecular weight identical to linear-4PEG (**2**).

The vapor pressure for two selected solvents, disub-3PEG (**7**) and disub-4PEG (**8**), were experimentally measured in the 1 L autoclave described above and were found to be negligible, with a maximum pressure of 71 Pa detected for (**7**) and 414 Pa for (**8**), respectively. Enthalpies were obtained from the plots of ln(P) vs 1/T for these solvents, but the results seemed too low to be credited. Siloxanes generally exhibit lower heats of vaporization, due to their very weak intermolecular interactions.[32-36] The extremely low vapor pressure of these solvents makes them highly sensitive to any errors involving small amounts of volatile impurities. Follow-up vapor pressure experiments will be performed at a different scale and using different equipment to obtain confidence in the results.

Computational Studies

An atomic level understanding of PEG-PDMS solvents can provide us further insight of their behavior, their interactions with CO_2, and can also help to design better solvents in the future. In this work, we used computational methods to calculate the charges on the atoms of PEG-PDMS molecules, interaction energies of different atom sites of PEG-PDMS with CO_2, and the free volume of PEG-PDMS solvents.

Charges on the atoms of PEG molecules provide insight into which atom sites interact most strongly with the CO_2. Because CO_2 acts as a Lewis acid, basic atom sites in the solvent molecules are expected to be locations of strongest interaction with CO_2. We found that the oxygen atoms of PEG-PDMS molecules were the basic sites (partially negatively charged), and charges on those sites are shown in the supplemental information (SI Figures 4-12). Sites with the maximum partial negative charge will possess the highest Lewis basicity and would be expected to be the sites where CO_2 interactions will be strongest. However, we show later that this is not the case because of steric effects.

The highest partial negative charges were always located within the siloxane head regardless of conformation or PEG length. The proximity of polarizable di- and trimethyl silane groups may account for the increased partial negative charges at these oxygens within these functionalities.

The highest partially negatively-charged O atoms in the PEG arms of linear and T-shaped molecules were consistently found at the second or third O atom removed from the siloxane core (Figure 4a, b). The higher partial negative charges tend to be closer to the siloxane core, while the smallest partial negative charge is always located at the terminal methoxy O atom. (Figure 4c). For all three conformations, the smallest partial negative charges for all O atoms in all molecules were consistently located at the terminal methoxy O atom.

However, further results predict that the location for strongest CO_2 approach was always at the terminal O atom in all nine solvents, which was contrary to the same atoms having the smallest partial negative charge. The CO_2 approach distance at this oxygen atom was always at the shortest distance, and CO_2 interaction energy at this location was always greatest at the terminus oxygen atom. These are shown in Figure 4 for linear (**1** - **3**) and T-shaped solvents (**4** - **6**). This seemingly contradictory result may be explained by the lack of steric crowding at the terminal oxygen atom due to the distance of the bulky siloxane unit. The bulky siloxane prevents the CO_2 from closely approaching the O atoms with higher partial negative charge but leaves the terminal O atom exposed. Calculations of CO_2 interactions with the larger disubstituted solvents (**7** - **9**) were too complex to be completed within a reasonable time frame and were not reported but were expected to follow a similar trend as reported for other solvents.

It has been suggested by Shi, et al.,[37] that it might be preferable, for solvents intended to separate CO_2 from other sparingly soluble gases like H_2, to have low molar volumes, and thus small FFV, to minimize the H_2 absorption while still maintaining a sufficiently high CO_2 solubility through chemical interactions from the PEG groups.[12] The FFV for each solvent are shown in Table 6. Solvents which were T-shaped (**4** - **6**) gave the largest FFV, as would be expected from the branched nature of their siloxane cores. The linear solvents (**1** - **3**) had slightly lower free volumes, and the disubstituted solvents (**7** - **9**) had the smallest amount of free volume. These calculated values were in general agreement with the experimental gas absorption data in Table 4 which shows that the disubstituted solvents tended to absorb less CO_2 than the linear or T-shaped analogues under similar conditions.

Solvent Foaming

Included among the physical properties listed in Table 2 is whether the solvent was observed to foam when exposed to gas. Early gas absorption experiments using T-4PEG (**5**) suffered from severe foaming problems across a variety of pressures and conditions. A simple test was performed on all 9 solvents in which a glass vial was filled with an aliquot of the solvent and shaken for 1 min, then observed immediately after, and again 1 min after the shaking had stopped.[38] This test is similar to tests described previously for aqueous surfactant solutions.[39-40] Solvents in which foam persisted after 1 min were considered to foam, and those in which the foam persisted over many minutes were considered to foam severely. These results are listed as such in Table 2.

A more rigorous foaming test was devised in which a 100 mL graduated cylinder was filled with 10 mL of solvent and N_2 was delivered through a gas diffusion tube at 1 L/min into samples of T-4PEG (**5**) and disub-4PEG (**8**). Images of this testing can be seen in Figure 5, in which the height of observed foam level during gas delivery was found to overflow the cylinder for T-4PEG (**5**). No such foaming was observed in the case of disub-4PEG (**8**).

The fact that linear- and T-4PEG foams (**2**, **5**), whereas disub-4PEG (**8**) does not is a matter of interest. Literature suggests that chemically-pure liquids such as those mentioned in this work should not foam,[41-43] as the coalescence occurs very rapidly when two or more bubbles come together to form foam.[44-45] However, some foaming is observed - although the foam is relatively unstable compared to the same liquids with surfactants present. Foaming occurs in pure liquids if there is the right balance of liquid properties including density, surface tension, viscosity, and whether sufficient turbulence is present to assist in the bubble formation. It has been previously reported that etheric groups, such as those found in all of the molecules reported here, are an effective way at reducing foaming,[46] but this only seems to be true for the disubstituted conformations. In this previous report it was revealed that a single long ether chain may lead to more effective micelle assembly than multiple shorter chains of similar length, so this may explain why the disubstituted molecules do not foam whereas the linear and T-shaped molecules with only a single PEG arm do.[46] Several alternative models are available in the literature to predict the foaming for different systems of both pure solvents and mixtures.[14, 47-48]

In the case of solvents discussed in this work, densities and surface tensions of all the solvents are almost identical, whereas viscosities of disubstituted molecules are almost twice that for the linear- and T-shaped conformations (Table 2). From these data, it can be postulated that the bubbles, and hence the persistent foams, are more difficult to form in solvents with higher viscosity where density and surface tension remain similar.

Visual observations of foaming behavior in a 4-L ZipperClave reactor were performed using three selected solvents: T-4PEG (**5**), disub-3PEG (**7**), and disub-4PEG (**8**). Experiments were conducted at a CO_2 flow rate of 0.0025 m^3/s and at temperatures of 20 and 40°C. Results comparing the foaming height and foam lifetime for the three solvents are shown in Figure 6. As can be seen in this figure, the measured results agree with the qualitative tests, in which the T-4PEG was observed to severely foam compared to the other two solvents, with the foam height up to 10 times larger than that of disub-3PEG and disub-4PEG. Moreover, it was observed that the very small amount of foam formed by disub-4PEG lasted longer than that of the shorter chain disub-3PEG (**7**) and the much larger foaming head formed by the T-4PEG (**5**).

Conclusions

A collection of nine analogous hybrid PEG-PDMS solvents were prepared in which the conformation (linear, T-shaped, and disubstituted) and length of PEG-substitution (with 3, 4, and 5 oxygen atoms) were systematically studied. Among them, the disubstituted conformations exhibited highly favorable gas separation characteristics and physical properties for the application of pre-combustion carbon capture. All nine solvents showed comparable CO_2 absorption at both 25 and 40°C, with the smallest PEG-substituted molecules consistently absorbing more CO_2 than the larger analogues due to lower viscosities.

The thermal decomposition temperature of the analogous hybrid PEG-PDMS solvents increased with increasing molecular weight for all three conformations. The volatility of the solvents was also tested at 80°C to estimate the amount of weight loss over time. The weight loss results for linear and T-shaped analogues showed the latter losing significantly more mass than the linear analogue, suggesting that while the T-shape imparts superior thermal stability, it is also more volatile despite having identical molecular weights.

Computational studies of the analogous hybrid PEG-PDMS solvents were performed, calculating partial negative charges as well as CO_2 interaction energies and distances for all O atoms located in these solvents. All nine molecules had the lowest partial negative charges at the terminal PEG O atom, yet this was consistently the site of the strongest CO_2 interaction. This surprising outcome must result from the lack of steric crowding at the terminal ether sites. The relative FFV were also computed and were found to be lowest for the disubstituted analogues, which will tend to result in higher CO_2/H_2 selectivity.

Finally, foaming behavior was studied for selected solvents and it was found that linear- and T-4PEG (**2**, **5**) exhibited foaming when exposed to flowing gas, but disub-4PEG (**8**) did not. These results were confirmed using quantitative experiments in a 4-L ZipperClave reactor, in which the height of the foam head was determined to be much larger for T-4PEG compared to disub-3PEG and disub-4PEG.

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Tables

Table 1. Chemical names of hydrophobic CO_2 capture solvents prepared.

Chemical name	Nickname	Formula
2,2,4,4,6,6-hexamethyl-3,5,10,13,16-pentaoxa-2,4,6-trisilaicosane (**1**)	linear-3PEG	$C_{15}H_{38}O_5Si_3$
2,2,4,4,6,6-hexamethyl-3,5,10,13,16,19-hexaoxa-2,4,6-trisilaicosane (**2**)	linear-4PEG	$C_{17}H_{42}O_6Si_3$
2,2,4,4,6,6-hexamethyl-3,5,10,13,16,19,22-heptaoxa-2,4,6-trisilatricosane (**3**)	linear-5PEG	$C_{19}H_{46}O_7Si_3$
2,2,4-trimethyl-4-((trimethylsilyl)oxy)-3,8,11,14-tetraoxa-2,4-disilapentadecane (**4**)	T-3PEG	$C_{15}H_{38}O_5Si_3$
2,2,4-trimethyl-4-((trimethylsilyl)oxy)-3,8,11,14,17-pentaoxa-2,4-disilaoctadecane (**5**)	T-4PEG	$C_{17}H_{42}O_6Si_3$
2,2,4-trimethyl-4-((trimethylsilyl)oxy)-3,8,11,14,17,20-hexaoxa-2,4-disilahenicosane (**6**)	T-5PEG	$C_{19}H_{46}O_7Si_3$
12,12,14,14,16,16-hexamethyl-2,5,8,13,15,20,23,26-octaoxa-12,14,16-trisilaheptacosane (**7**)	disub-3PEG	$C_{22}H_{52}O_8Si_3$
15,15,17,17,19,19-hexamethyl-2,5,8,11,16,18,23,26,29,32-decaoxa-15,17,19-trisilatritriacontane (**8**)	disub-4PEG	$C_{26}H_{60}O_{10}Si_3$
18,18,20,20,22,22-hexamethyl-2,5,8,11,14,19,21,26,29,32,35,38-dodecaoxa-18,20,22-trisilanonatriacontane (**9**)	disub-5PEG	$C_{30}H_{68}O_{12}Si_3$

Table 2. Physical properties of hydrophobic CO_2 capture solvents prepared. Errors reported (2σ) are for 5 replicate measurements at the temperatures stated.

product	FW, g/mol	density, g/mL at 25.0°C	viscosity, mPa·s at 30.0°C	foam?
linear-3PEG (**1**)	382.7	0.92056 ± 0.00003	3.345 ± 0.478	severe
linear-4PEG (**2**)	426.8	0.93342 ± 0.00001	4.666 ± 0.027	severe
linear-5PEG (**3**)	470.8	0.95594 ± 0.00005	6.272 ± 0.349	no
T-3PEG (**4**)	382.7	0.91814 ± 0.00005	3.582 ± 0.228	yes
T-4PEG (**5**)	426.8	0.94236 ± 0.00003	5.253 ± 0.012	yes
T-5PEG (**6**)	470.8	0.95197 ± 0.00003	6.541 ± 0.196	no
disub-3PEG (**7**)	528.9	0.97081 ± 0.00003	7.154 ± 0.146	no
disub-4PEG (**8**)	617.0	0.98994 ± 0.00003	12.85 ± 0.082	no
disub-5PEG (**9**)	705.1	1.00554 ± 0.00003	15.97 ± 0.346	no

Table 3. Comparison of CO_2 absorption plot linear fit slopes from TGA data achieved by hydrophilic carbon capture solvents at 25 and 40°C (see Figure 2). Correlation coefficients and average absolute percent deviations (AAPD) are included.

25°C data	linear fit slope, mol/L·bar	normalized slope*	r^2	AAPD
linear-3PEG (**1**)*	0.1422	1.000	0.994	9.07
linear-4PEG (**2**)	0.1319	0.928	0.994	1.53
linear-5PEG (**3**)	0.1354	0.952	0.996	6.99
T-3PEG (**4**)	0.1363	0.959	0.997	6.59
T-4PEG (**5**)	0.1282	0.902	0.994	1.72
T-5PEG (**6**)	0.1371	0.964	0.997	5.36
disub-3PEG (**7**)	0.1377	0.968	0.998	5.21
disub-4PEG (**8**)	0.1233	0.889	0.995	1.43
disub-5PEG (**9**)	0.1337	0.940	0.998	5.60

40°C data	linear fit slope, mol/L·bar	normalized slope*	r^2	AAPD
linear-3PEG (**1**)	0.0977	0.990	0.999	5.07
linear-4PEG (**2**)	0.0955	0.968	0.999	0.84
linear-5PEG (**3**)	0.0897	0.909	0.999	5.47
T-3PEG (**4**)*	0.0987	1.000	0.999	3.72
T-4PEG (**5**)	0.0917	0.929	0.997	1.62
T-5PEG (**6**)	0.0959	0.972	0.999	3.69
disub-3PEG (**7**)	0.0974	0.987	0.999	2.49
disub-4PEG (**8**)	0.0889	0.901	0.999	0.93
disub-5PEG (**9**)	0.0935	0.947	0.994	4.25

Table 4. Comparison of CO_2 absorption slopes achieved by hydrophilic carbon capture solvents prepared at 25 and 40°C, with data normalized to the highest slope for each temperature and organized according to conformation (see Figure 2).

T= 25°C data	normalized slope	slope range	T= 40°C data	normalized slope	slope range
<u>structure</u>			<u>structure</u>		
avg linear	1	2.9%	avg T	1	2.3%
avg T	0.981		avg linear	0.988	
avg disub	0.971		avg disub	0.978	

Table 5. Decomposition temperatures and evaporation rates at 80°C of hydrophobic CO_2 capture solvents.

product	T_{dec}, °C	wt% lost/hr at 80°C	wt% lost/day at 80°C
linear-3PEG (**1**)	209	7.25	>100
linear-4PEG (**2**)	222	2.79	66.96
linear-5PEG (**3**)	227	0.875	21.01
T-3PEG (**4**)	221	9.58	>100
T-4PEG (**5**)	222	3.61	86.67
T-5PEG (**6**)	243	1.17	28.09
disub-3PEG (**7**)	238	0.734	17.62
disub-4PEG (**8**)	248	0.562	13.48
disub-5PEG (**9**)	258	0.405	9.72

Table 6. Calculated fractional free volumes of hydrophobic CO_2 capture solvents.

product	FFV	Normalized FFV
linear-3PEG (**1**)	0.21454	0.9994
linear-4PEG (**2**)	0.20518	0.9558
linear-5PEG (**3**)	0.19855	0.9249
T-3PEG (**4**)	0.21467	1.0000
T-4PEG (**5**)	0.20999	0.9782
T-5PEG (**6**)	0.19855	0.9249
disub-3PEG (**7**)	0.19361	0.9019
disub-4PEG (**8**)	0.18451	0.8595
disub-5PEG (**9**)	0.18308	0.8528