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CO₂ Solubility in Organophosphate Physical Solvents Wherein Alkyl Groups Are Replaced with Poly(Ethylene Glycol) Groups

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Abstract

Previous success in improving the CO₂ capacity of physical solvents for pre-combustion carbon capture by imparting poly(ethylene glycol) (PEG) functionality led us to compare tributyl phosphate (TBP), tri-isobutyl phosphate (T’BP) and three analogous organophosphate solvents in which the length of PEG-substitution was varied. The PEG-substituted solvents proved to have acceptable densities and viscosities for the application of interest, but all three solvents showed poorer CO₂ absorption than TBP or T’BP. Inclusion of hydrophilic PEG groups in solvents (1) – (3) also led to the undesired absorption of larger amounts of water from humidified N₂ compared to TBP and T’BP. Computational studies of the analogous organophosphate solvents revealed that all solvents had the lowest partial negative charges, closest CO₂ interaction, and largest CO₂ interaction energy at the double bonded phosphoryl O atom. The fractional free volumes were computed and was found to be largest for T’BP and grew progressively smaller as the length of the PEG group grew longer in solvents (1) – (3). Although introducing PEG groups to these molecules increased the number of interaction sites with CO₂, solvents (1) – (3) showed poorer CO₂ absorption than TBP and T’BP due to their decreased solvent fractional free volume.

Introduction

Carbon capture and storage from fossil-based power generation is a critical component of realistic strategies for preventing a further rise in atmospheric CO₂ concentrations. However, capturing meaningful amounts of CO₂ using current technology could result in a prohibitive rise in the cost of electric power consumed. One strategy to minimize energy consumption and economic penalties is to exploit industrial streams in which CO₂ is already at high partial pressures, such as the syngas exiting coal gasifiers at integrated gasification combined cycle (IGCC) power plants. In these high-pressure CO₂-containing streams, one well-established approach to removing acid gases (CO₂ and H₂S) from the syngas stream is the use of physical solvents.[1]

The physical solvents used in pre-combustion capture of CO₂ from coal-gasified power plants are typically more effective at high pressures than chemical solvents.[2] Physical solvents that have been studied for CO₂ absorption include N-methyl-2-pyrrolidone (NMP - Purisol), propylene carbonate (Fluor solvent),[3] methanol (Rectisol),[4] and dimethyl ethers of polyethylene glycol (Selecol).[5,6]

One physical solvent that had been studied earlier, but was then seemingly neglected, is tributyl phosphate (TBP), originally identified in the Esasolvan process.[7] This solvent was used for natural gas purification and while it showed only moderate capacity to absorb CO₂, it was an excellent solvent for absorbing H₂S and SO₂.[8,9] The inclusion of etheric side chains in the form
of poly(ethylene glycol) (PEG) units of varying lengths has been shown to impart favorable gas absorption selectivities for CO$_2$ over CH$_4$ and N$_2$, while maintaining good CO$_2$ solubilities and other physical properties for imidazolium ionic liquids by Bara, et al.[10-12] Previously we reported on this approach as being successful for a novel liquid solvent, PEG-Siloxane-1, which is a hybrid solvent of PEG and poly(dimethyl siloxane) (PDMS).[13] and in other recent work.[14] This approach has greatly improved the CO$_2$ absorption capacity and CO$_2$/H$_2$ selectivity of these solvents and therefore was of interest to impart similar properties to TBP.

Research reported by Hess, et al.[15] has shown that organophosphates with PEG substituents are excellent liquid electrolyte media with useful properties including high boiling points and low viscosities, which also render them excellent candidates as CO$_2$ solvents. They reported the synthesis[16,17] of two symmetrical organophosphates from 2-methoxyethan-1-ol and diethylene glycol, monomethyl ether, respectively, which we identified for study.

In this work we report the synthesis of these two products, which we refer to as OP(1PEG)$_3$ (1 - tris(2-methoxyethyl) phosphate) and OP(2PEG)$_3$ (2 - tris(2-(2-methoxyethoxy)ethyl) phosphate), as well as a third homologous product OP(3PEG)$_3$ (3 - tris(2-(2-methoxyethoxyethoxy)ethyl) phosphate) prepared using triethylene glycol, monomethyl ether. Herein, we report the physical properties, water absorption, thermal properties, and CO$_2$ absorption behavior of these three solvents and use computational results to describe their performance in comparison to TBP and its structural isomer tri-isobutyl phosphate (T'BP).

**Experimental**

**Syntheses**

The preparation of the solvents discussed in this work were accomplished by way of a reaction between POCl$_3$ and an excess of alcohol catalyzed by 4-dimethylaminopyrididine in dichloromethane (DCM); all reagents were used as received from Sigma Aldrich. The method of preparation of these compounds was derived from reactions reported by Hess, et al.[15-17] The solvents prepared in this work are shown in Figure 1. Three symmetrical solvents with different lengths of PEG-substituted side-chains were prepared, with their physical properties listed in Table 1 along with TBP and T'BP.

**Synthesis of tris(2-methoxyethyl) phosphate (1):** A 500 mL round bottomed flask was charged with 2-methoxyethan-1-ol (62.3 g, 819 mmol, 4.16 equiv.), triethylamine (85.9 g, 849 mmol, 4.32 eq), and 4-dimethylaminopyridine (2.12 g, 17.4 mmol, 0.10 eq) dissolved in 200 mL DCM. The resultant homogeneous solution was cooled to 0°C in an ice bath and slowly treated drop-wise with phosphorus oxychloride (30.2 g, 197 mmol, 1 eq) dissolved in 100 mL DCM. The rate of dropping was controlled to occur over 60 min time with the temperature maintained around 0°C during which the clear reaction solution eventually became cloudy white. The resultant solution was left to stir at room temperature overnight. This solution was filtered to remove triethylamine hydrochloride, and the yellow DCM solution was washed twice with 300 mL 5% HCl and then 400 mL water. The organic layer was isolated and evaporated to give an off-white liquid, which was vacuum distilled to give a clear colorless liquid. $^1$H NMR (CDCl$_3$): δ ppm 4.11 (m, OCH$_2$CH$_2$O, 6H), 3.52 (m, OCH$_2$CH$_2$O, 6H), 3.30 (m, OCH$_3$, 9H). $^{13}$C NMR (CDCl$_3$): δ ppm 71.0 (d, 3C), 66.4 (d, 3C), 70.6 (s, 3C), 58.6 (s, 3C). $^{31}$P NMR (CDCl$_3$): δ ppm -0.92. ESI MS: calc’d for C$_9$H$_{22}$O$_7$P
Synthesis of tris(2-(2-methoxyethoxy)ethyl) phosphate (2): A method similar to that described for (1) was employed using diethylene glycol, monomethyl ether (130 g, 1082 mmol, 4.04 equiv.), triethylamine (114 g, 1127 mmol, 4.20 eq), and 4-dimethylaminopyridine (2.62 g, 21.4 mmol, 0.08 eq) dissolved in 250 mL DCM and phosphorus oxychloride (41.1 g, 268 mmol, 1 eq) dissolved in 100 mL DCM. The crude product was vacuum distilled to give a clear colorless liquid. $^1$H NMR (CDCl$_3$): $\delta$ ppm 4.10 (m, OCH$_2$CH$_2$O, 6H), 3.61 (m, OCH$_2$CH$_2$O, 6H), 3.54 (m, OCH$_2$CH$_2$OMe, 6H), 3.43 (m, OCH$_2$CH$_2$OMe, 6H), 3.26 (m, OCH$_3$, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ ppm 71.6 (s, 3C), 70.2 (s, 3C), 71.6 (s, 3C), 70.2 (s, 3C), 69.7 (d, 1C), 66.4 (d, 3C), 58.7 (s, 3C). $^{31}$P NMR (CDCl$_3$): $\delta$ ppm -1.13. ESI MS: calc’d for $\text{C}_{15}$H$_{34}$O$_{10}$P (M+H)$^+$ 405.39756, found 405.18692; calc’d for $\text{C}_{15}$H$_{34}$NaO$_{10}$P (M+Na)$^+$ 427.37950, found 427.16957.

Synthesis of tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) phosphate (3): A method similar to that described for (1) was employed using triethylene glycol, monomethyl ether (129 g, 783 mmol, 4.00 equiv.), triethylamine (84.3 g, 828 mmol, 4.23 eq), and 4-dimethylaminopyridine (2.06 g, 18.6 mmol, 0.09 eq) dissolved in 250 mL DCM and phosphorus oxychloride (30.1 g, 196 mmol, 1 eq) dissolved in 100 mL DCM. The crude product was vacuum distilled to give a clear colorless liquid. $^1$H NMR (CDCl$_3$): $\delta$ ppm 4.11 (m, OCH$_2$CH$_2$O, 6H), 3.62-3.54 (br m, OCH$_2$CH$_2$O, 24H), 3.54 (m, OCH$_2$CH$_2$OMe, 6H), 3.29 (m, OCH$_3$, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ ppm 71.7 (s, 3C), 70.2 (s, 3C), 70.4 (s, 6C), 70.3 (s, 3C), 69.7 (d, 3C), 66.5 (d, 3C), 58.7 (s, 3C). $^{31}$P NMR (CDCl$_3$): $\delta$ ppm -1.05. ESI MS: calc’d for $\text{C}_{21}$H$_{49}$NO$_{13}$P (M+NH$_4$)$^+$ 554.58178, found 554.29290; calc’d for $\text{C}_{21}$H$_{49}$NaO$_{13}$P (M+Na)$^+$ 559.53718, found 559.24831.

Synthesis of TIBP: A method similar to that described for (1) was employed using isobutyl alcohol (85.0 g, 1146 mmol, 4.27 equiv.), triethylamine (115 g, 1137 mmol, 4.24 eq), and 4-dimethylaminopyridine (2.58 g, 21.1 mmol, 0.08 eq) dissolved in 250 mL DCM and phosphorus oxychloride (41.1 g, 268 mmol, 1 eq) dissolved in 100 mL DCM. The crude product was vacuum distilled to give a clear colorless liquid. $^1$H NMR (CDCl$_3$): $\delta$ ppm 3.72 (dt, OCH$_2$CH, 6H), 1.88 (m, CH$_2$CH(CH$_3)_2$, 3H), 0.87 (d, CH(CH$_3)_2$, 18H). $^{13}$C NMR (CDCl$_3$): $\delta$ ppm 73.3 (d, 3C, OCH$_2$CH), 28.9 (d, 3C, CH$_2$CH(CH$_3)_2$), 18.5 (s, 6C, CH(CH$_3)_2$). $^{31}$P NMR (CDCl$_3$): $\delta$ ppm -0.97. ESI MS: calc’d for $\text{C}_{12}$H$_{20}$O$_4$P (M+H)$^+$ 267.17197, found 267.17240; calc’d for $\text{C}_{12}$H$_{27}$NaO$_4$P (M+Na)$^+$ 289.15447, found 289.15400.
Figure 1. Molecular structures of TBP, T'Bp, and the three PEG-solvents prepared in this study: OP(1PEG)₃ (1), OP(2PEG)₃ (2), and OP(3PEG)₃ (3).

**Instrumentation**

Density measurements were completed on a Rudolph Research Analytical DDM 2911 automatic density meter at 25°C; all samples were measured with five replicates and the average density was reported. Viscosity measurements were performed on a Rheosense model µVisc microviscometer outfitted with a temperature controller set to 25°C; all samples were measured with five replicates and the average viscosity was reported. Moisture content was determined using a Metrohm Titrando Karl Fisher titration system at 120°C using 50 mL/min N₂ gas flow in oven mode; all samples were measured as three replicates and the average moisture content was reported.

TGA analyses were collected on a TA Instruments SDT-Q600 using 50 mL/min air as a sweep gas. 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 ¹H and ¹³C NMR spectra were referenced to their respective solvent resonances.

**Gas Absorption Experiments**

Gravimetric CO₂ adsorption measurements were conducted on a Hiden IGA-001 microbalance. Samples (30-50 mg) were activated by purging with CO₂ at 70 mbar at 40°C until the sample weight stabilized. Isotherms were then measured under flowing CO₂ 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 minor correction (<5% of the adsorbed mass at 18 bar) 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 CO₂ adsorption.[18,19]
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). Shiflett and Yokozeki employed a similar system to measure equilibrium CO$_2$ absorption in ionic liquids and estimated the relative uncertainty in CO$_2$ pressure to be 0.008 bar and in mole fraction CO$_2$ solubility to be less than 0.006.[20]

Water vapor adsorption measurements were conducted using an inline humidifier which was held at 23°C with a sample temperature of 25°C with N2 as the carrier gas. The relative humidity in the gas stream was controlled by blending dry N$_2$ with humidified N$_2$ prior to entering the sample chamber with the gas ratios set using mass flow controllers. Relative humidity in the sample chamber was then calculated from the sample chamber temperature and vapor pressure of water in the humidifier assuming complete saturation of the carrier gas. Final equilibrium loading of water vapor in the sample was determined by fitting the water adsorbed sample mass to an asymptotic model using OriginPro® (v 9.1) curve fitting software.

Computational Details
Ab initio 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 by using B3LYP/6-311++g(d,p) followed by charge calculations by using the CHELPG protocol.[21] The CO$_2$-molecule dimer was also optimized by using B3LYP/6-311++g(d,p) followed by a 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.[22,23] All ab initio calculations were performed by using the Gaussian 09 program.[24] All fractional free volume calculations were calculated by using a modified Bondi method,[25] which has been implemented in an in-house software package at NETL. We have reported further details on this method in our previous work.[14]

Results and Discussion
Physical Properties
Physical properties for all solvents studied are listed in Table 1. The density of TBP is slightly higher than TBP due to the presence of branched alkyl groups in the latter. The solvent density increases by 15% going from TBP to OP(1PEG)$_3$ (1); the densities then decrease slightly with the addition of increasingly longer PEG arms in (2) and (3). The viscosity of TBP is slightly lower than TBP and the viscosity of (1) was roughly double that of TBP, with viscosity increasing by a factor of two with each addition of increasingly longer PEG arms. The water content after drying for all molecules was consistently low, despite having been thoroughly water-washed; again, the water content increased slightly with the addition of increasingly longer PEG arms due to the presence of additional hydrophilic ether groups.
Table 1. Physical properties of PEG-substituted organophosphate solvents prepared.

| product         | FW, g/mol | density, g/mL at 25°C | viscosity, cP at 25°C | H₂O content, ppm |
|-----------------|-----------|-----------------------|-----------------------|------------------|
| TBP             | 266.31    | 0.9728                | 3.84 ± 0.06           | 926              |
| T'BP            | 266.31    | 0.9618                | 4.75 ± 0.02           | 2202             |
| OP(1PEG)₀ (1)   | 272.23    | 1.161                 | 7.89 ± 0.04           | 1143             |
| OP(2PEG)₀ (2)   | 404.39    | 1.149                 | 18.9 ± 0.08           | 3352             |
| OP(3PEG)₀ (3)   | 536.55    | 1.143                 | 34.3 ± 0.48           | 3507             |

Spectroscopic Properties
The FTIR spectra of all four phosphate molecules were recorded and the frequency for phosphoryl group vibration was observed to shift slightly upwards as the length of the substituent groups increased (Table 2). This is consistent with results reported by Wagner, who related this trend to decreasing O-P bond order as the electronegativity of the ester group increases.[26] The presence of more O atoms in the ester groups withdraws electrons away from the phosphorus atom, which compensates by increasing the bond order in the phosphoryl π-bond. The downward shift of 5 cm⁻¹ going from TBP to T'BP suggests that the branched butyl groups are slightly more electron donating than linear groups, leading to a small decrease in P=O bond order.

Table 2. Spectroscopic properties of PEG-substituted organophosphate solvents prepared.

| product         | FTIR ν(O=P), cm⁻¹ | ³¹P NMR δ, ppm in CDCl₃ |
|-----------------|--------------------|------------------------|
| TBP             | 1263               | -0.72                  |
| T'BP            | 1258               | -0.97                  |
| OP(1PEG)₀ (1)   | 1263               | -0.92                  |
| OP(2PEG)₀ (2)   | 1269               | -1.13                  |
| OP(3PEG)₀ (3)   | 1272               | -1.05                  |

The ³¹P NMR spectra for all four phosphate molecules were also noted, and the chemical shifts tended to shift upfield as the length of the substituent groups increased (also Table 2). This is also consistent with results reported by Gorenstein, who related this trend to increasing O-P-O bond angles in phosphate esters.[27,28] Substituents with greater steric bulk force themselves further apart, leading to larger O-P-O bond angles, which more effectively shields the ³¹P nucleus.

CO₂ Absorption
The PEG-substituted solvents prepared in this work, TBP, and T'BP were tested for CO₂ absorption at 25 and 40°C, using CO₂ pressures from 0 to 20 bar on the Hiden microbalance. Plots of moles of CO₂ dissolved per liter versus CO₂ pressure are illustrated in Fig. 2, with the linear fit for the highest slope (T'BP at both temperatures) shown by a dashed line. Higher capacity for CO₂ absorption is reflected in larger slopes for the linear fit for these plots. The slope and correlation coefficient for each solvent at both temperatures are listed in Table 3. These plots were all linear ($r^2 ≥ 0.997$) throughout the pressure ranges tested (0 to 10 bar).
Figure 2. CO₂ absorption results measured by gravimetric Hiden microbalance at (a) 25°C and (b) 40°C for (1) - (3), TBP, and T'BP.

Table 3. Comparison of CO₂ absorption plot linear fit slopes from gravimetric Hiden microbalance data and correlation coefficients achieved by TBP, T'BP, and PEG-substituted organophosphate solvents at 25 and 40°C.

|           | Linear fit slope, mol/L bar | Normalized slope | r²   |
|-----------|-----------------------------|------------------|------|
| 25°C data |                             |                  |      |
| TBP       | 0.1404                      | 1.000            | 0.9987 |
| T'BP      | 0.1419                      | 1.011            | 0.9989 |
| OP(1PEG)₃ (1) | 0.1250                | 0.890            | 0.9991 |
| OP(2PEG)₃ (2) | 0.1158              | 0.825            | 0.9978 |
| OP(3PEG)₃ (3) | 0.1138                | 0.811            | 0.9986 |
| 40°C data |                             |                  |      |
| TBP       | 0.1021                      | 1.000            | 0.9998 |
| T'BP      | 0.1065                      | 1.043            | 0.9997 |
| OP(1PEG)₃ (1) | 0.0922                 | 0.903            | 0.9998 |
| OP(2PEG)₃ (2) | 0.0862              | 0.844            | 0.9998 |
| OP(3PEG)₃ (3) | 0.0832                | 0.815            | 0.9994 |

It was observed that CO₂ was most soluble in T'BP at both temperatures. The CO₂ solubility decreased slightly going from T'BP to TBP and decreased more significantly going from TBP to (1). The CO₂ solubility continued decreasing as the PEG arm grew longer for (2) and (3), with CO₂ absorption decreasing by as much as 10% for (3) at both temperatures. We have observed similar CO₂ absorption results when varying the PEG arm lengths in hybrid PEG/siloxane CO₂ solvents, where shorter PEG substituents tended to have higher CO₂ absorption.[13] But unlike those hybrid solvents, the inclusion of etheric groups failed to improve CO₂ uptake.
Absorption of Moisture

TBP and solvents (1) through (3) were exposed to moisture over a two-week period and the change in sample weight and water content was determined. An acrylic desiccator cabinet had two holes drilled into it on opposite sides and was fitted with plastic hose barbs. The cabinet was then purged with N₂ flowing through a gas bottle filled with water. The cabinet was able to maintain a relative humidity of around 80% under these conditions, as measured by a Dwyer Series 485 digital hygrometer. Glass vials were loaded with 1 g each of solvent, weighed, and stored with their caps off inside the humidification chamber. The weights were recorded once during the two-week test span and at the end of the experiment; the water content was determined by Karl Fisher titration before and after the two-week span.

Figure 3 shows the change in mole % water for TBP and (1) – (3), where the percentages have been normalized to the starting water content of the solvents. As the lengths of the PEG-substituents increases, the mole % water also increases steadily. The increase in mole % water exceeds three orders of magnitude for (3). The amount of water measured by Karl Fisher titration after humidification was consistent for all three PEG-substituted solvents at 40 wt % after two weeks exposure. The tendency of etheric groups to increase the hydrophilic character of molecules has been documented by Menger and Chlebowski, who reported that etheric surfactants show less tendency to self-aggregate and are less likely to adsorb onto hydrophobic surfaces than similar surfactants lacking ether groups.[29]

Figure 3. Plot of change in mole % water versus time spent in the humidification chamber for (1) - (3), and TBP.

TBP, T’BP, and the PEG-substituted solvents prepared in this work were also tested for water absorption on the Hiden microbalance using humidified N₂. Plots of moles of H₂O absorbed per liter versus relative humidity are illustrated in Figure 4. TBP and T’BP were observed to absorb nearly identical amounts of water, taking up only 2 mol/L at 90% relative humidity. The PEG-
substituted solvents were observed to take up nearly identical amounts of water under these conditions, at levels more than 4 times larger than TBP or T'BP. It is interesting that (1) – (3) show an exponential-type increase in water absorption with increasing humidity, while TBP and T'BP do not. Increasing numbers of etheric O atoms provide more water interaction sites in solvents (1) – (3). Thus, both the CO₂ and H₂O absorption properties of these functionalized TBP analogues become less favorable upon inclusion of etheric groups.

Figure 4. Water absorption results from humidified N₂ as measured by gravimetric Hiden microbalance at 25°C for (1) - (3), TBP, and T'BP.

Thermal Properties
All five solvents were studied by thermal gravimetric analysis (TGA) to determine the thermal stability of the various conformations. A small aliquot of each molecule (ca. 15-20 mg) was loaded into an alumina TGA pan and temperature was ramped to 750°C at 10°C/min under 100 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 4, which shows that the decomposition temperature increases with increasing molecular weight for all four solvents.

Table 4. Thermal properties of TBP and PEG-substituted organophosphate solvents.

| product             | T_{dec}, °C | wt% lost/hr at 80°C | wt% lost/day at 80°C |
|---------------------|-------------|---------------------|----------------------|
| TBP                 | 214         | 9.18                | >100                 |
| T'BP                | 157         | 19.5                | >100                 |
| OP(1PEG)_3 (1)      | 235         | 2.09                | 50.1                 |
| OP(2PEG)_3 (2)      | 294         | 0.504               | 12.1                 |
| OP(3PEG)_3 (3)      | 319         | 0.324               | 7.78                 |
The solvents were also tested for longer term thermal stability (as an approximation of their tendency to evaporate) by exposing aliquots to 80°C temperatures for two days under 50 mL/min air flow to estimate the amount of weight loss to be expected due to volatility. These results are also listed in Table 4, and the results show that the weight lost decreases with increasing molecular weight, as shown in Figure 5. Both (2) and (3) lost approximately 10 wt% over the two-day span, whereas (1) lost almost 90 wt%, and both TBP and TiBP had completely evaporated during this time. Unlike the CO₂ and H₂O absorption properties, the tendency of these functionalized TBP analogues to evaporate improved upon inclusion of etheric groups.

![Figure 5. Evaporation of (1) - (3), TBP, and TiBP in 50 mL/min air at 80°C as monitored by TGA.](image)

**Computational Studies**

An atomic level understanding of carbon capture solvents can provide us further insight of their behavior and can help to design better solvents in the future. In this work, we used computational methods to calculate the partial atomic charges on the O atoms of TBP, TiBP, and (1) – (3), the interaction energies of these different atom sites with CO₂, and the fractional free volume of these solvents.

Computational calculations were performed to calculate the amount of negative charge on all oxygen atoms in the solvents prepared in this study. Results for all four molecules in this study are shown in Figure 6. These calculations reveal that the highest negative charges were always located on the phosphoryl O, regardless of PEG-arm length or butyl group branching. This negative charge was largest for (2) and was smallest for TiBP. The negative charges on the phosphoryl O of all the solvent molecules are very close, and the small differences of charges in molecules (1) – (3) could be attributed to the vicinity atoms of phosphoryl O in the optimized structures.
Figure 6. Calculated negative charges on oxygen atoms (1) - (3), TBP, and T’BP.

The charges on the O atoms in the PEG arms tended to decrease with distance removed from the phosphoryl group. In (1) and (2) the charges consistently decreased away from the phosphoryl group, whereas in (3) they were slightly elevated at the two internal etheric O atoms. For all three phosphate esters, the lowest negative charges for all O atoms in all molecules were consistently located at the terminal methoxy O atom. These results suggest that the phosphoryl group is the most likely location for interaction with CO$_2$, even when PEG groups are present.

Further results agreed that the location for strongest CO$_2$ approach was always at the phosphoryl O atom in all five solvents. The CO$_2$ approach distance at this oxygen atom was always at the shortest distance and the CO$_2$ interaction energy at this location was always largest. These are shown in Figure 7. CO$_2$ approach distance and interaction energies were only slightly less favorable at the terminal methoxy O atoms of (1) – (3) but were significantly less favorable at the internal etheric O atoms. This is likely influenced by the steric bulk of the PEG arms making approach of the internal O atoms by CO$_2$ more difficult. This also explains why adding etheric groups to TBP fails to improve CO$_2$ absorption: the primary interaction site is always at the phosphoryl O atom, where the interaction is far stronger than at any ether O atom.
It has been suggested by Shi, et al.[30] 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 fractional free volumes (FFV), to minimize the H$_2$ absorption while still maintaining a sufficiently high CO$_2$ solubility through chemical interactions with functional groups.[11] Free volume is related to the density and molar volume of the solvent. Computational results for the FFV for each solvent are shown in Table 5. TBP gave the largest FFV, as would be expected due to the branched nature of the isobutyl groups. The FFV of (1) – (3) steadily decreased as the PEG arms grew longer. These calculated values were in general agreement with the experimental gas absorption data in Table 3 which shows that the molecules with longer PEG arms absorbed less CO$_2$ while branched T’BP absorbed slightly more CO$_2$ than linear TBP. As seen in Figure 8, a plot of the 25°C CO$_2$ absorption capacity versus solvent FFV showed a linear relationship ($r = 0.9945$), suggesting that FFV is the dominant factor in CO$_2$ absorption in these solvents. Although introducing PEG groups to these molecules increased the number of interaction sites with CO$_2$, solvents (1) – (3) showed poorer CO$_2$ absorption than TBP and T’BP due to decreased solvent FFV.

Table 5. Calculated solvent FFV for TBP, T’BP, and PEG-substituted organophosphates.

| product          | FFV  | Normalized FFV |
|------------------|------|----------------|
| TBP              | 0.2247 | 1.000         |
| T’BP             | 0.2335 | 1.039         |
| OP(1PEG)$_3$ (1) | 0.1799 | 0.800         |
| OP(2PEG)$_3$ (2) | 0.1644 | 0.731         |
| OP(3PEG)$_3$ (3) | 0.1561 | 0.695         |
Conclusions

Previous success in improving the usefulness of physical carbon capture solvents by imparting PEG functionality led us to compare TBP, TBP and three analogous organophosphate solvents in which the length of PEG-substitution was varied. The PEG-substituted solvents (1) – (3) proved to have acceptable densities and viscosities, but all three solvents showed poorer CO₂ absorption at both 25 and 40°C than TBP or TBP. Inclusion of hydrophilic PEG groups in solvents (1) – (3) also led to the undesired absorption of larger amounts of water from humidified N₂ compared to TBP and TBP. The thermal decomposition temperature of the PEG-substituted solvents increased with increasing molecular weight for all three solvents. Study of the evaporation at 80°C for solvents (1) – (3) showed them losing significantly less mass than TBP or TBP.

Computational studies of the analogous organophosphate solvents were performed, calculating partial negative charges as well as CO₂ interaction energies and distances for all O atoms located in these solvents. All five molecules had the lowest partial negative charges, closest CO₂ interaction, and largest CO₂ interaction energy at the phosphoryl O atom. The addition of etheric groups to TBP fails to improve CO₂ absorption because the additional ether groups have CO₂ interactions which are much smaller than with the phosphoryl group. The solvent FFV were computed and was found to be largest for TBP and grew progressively smaller as the length of the PEG group grew longer in solvents (1) – (3). It was concluded that FFV was the dominant factor for determining CO₂ absorption ability in organophosphate solvents.

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