A challenge for green chemistry: designing molecules that readily dissolve in carbon dioxide

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Carbon dioxide is a green yet feeble solvent whose full potential won't be realized until we develop a more thorough understanding of its solvent behavior at the molecular level. Fortunately, advances in molecular modeling coupled with experiments are rapidly improving our understanding of CO_2's behavior, permitting design of new, more sustainable "CO_2-philes".

Carbon dioxide is considered to be a "green" solvent, and hence substantial effort has been devoted to developing process applications for carbon dioxide that replace the use of other, more hazardous solvents.[1] Unfortunately, CO_2 is a feeble solvent;[2] although it can solubilize low-molecular weight, volatile compounds at pressures below 100 bar, polar and high-molecular weight materials are usually poorly soluble at tractable pressures. An ability to *a priori* design highly CO_2-soluble ("CO_2-philic") compounds would advance the "greening" of demanding yet important applications in various industries. It is somewhat ironic that while molecular attributes required to allow dissolution in water (our "other" green solvent) are relatively obvious, a full understanding of the solvent character of CO_2 remains a challenge. CO_2's solvent power has in the past been likened to that of toluene based on FT-IR spectroscopy, to hexane and to pyridine based on thermodynamic solubility parameter calculations, and to acetone based on hydrogen bond accepting tendency. These descriptions have all been discarded over the years as experimental data has revealed them to be oversimplifications. Indeed, recent work by Bush and colleagues[3] suggests that CO_2 exhibits "multiple solvent personalities", in that one of CO_2's three MOSCED solvent parameters[4] suggests a resemblance to perfluorohexane, another to acetone, and the third to acetonitrile. CO_2 clearly has great potential as a green solvent, but a thorough fundamental understanding of its

behavior is needed to take full advantage of its properties.

Designing CO_2-philic compounds: what can we learn from fluoropolymer behavior?

By the end of the 1980's, the scientific community had all but dismissed CO_2's potential as a process solvent owing to its weak solvent strength. In 1992, however,

DeSimone and colleagues[5] published the first report of a truly "CO_2-philic" material, when they showed that a poly(perfluoroalkyl acrylate) (Poly(FOA); see Fig. 1) with over 2500 repeat units was miscible with CO_2 at pressures below 150 bar. By contrast, Heller and colleagues[6] had earlier noted that typical non-fluorinated polymers with fewer than 25 repeat units were *insoluble in CO_2 at 200 bar*. Subsequent work showed that

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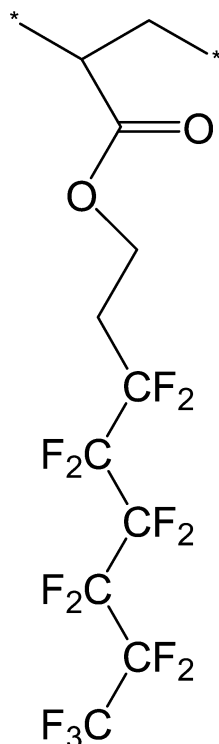
Fig. 1 Repeat unit structure of poly(FOA).

attachment of fluorinated "ponytails" to chelating agents, surfactants, and catalyst ligands generally enhanced the solubility of such compounds in CO_2.[1] The problem of CO_2's weak solvent strength seemed to have been solved; *fluorination = CO_2-philicity*.

Unfortunately, the use of fluorinated ponytails to achieve CO_2 solubility is relatively expensive, and towards the end of the 1990's, it also became somewhat environmentally problematic. More interesting from our point of view, however, were the reports in the literature showing that the heuristic, "*fluorination = CO_2-philicity*" was not quite correct. Some, but interestingly not all fluorinated alkane, acrylate and ether polymers are miscible with CO_2 at much lower pressures than their non-fluorous counterparts. Attempts to explain the CO_2-philic character of fluorinated CO_2-philes have focused on determining whether there exist any specific interactions between CO_2 and these molecules. Yee *et al.* used FTIR to investigate mixtures of CO_2 and hexafluoroethane,[7] finding no evidence of specific attractive interactions between the F atoms and CO_2. The authors consequently attributed the observed enhanced solubility of fluorocarbons to weak solute–solute interactions. However, when Dardin *et al.* compared ^{1}H and ^{19}F NMR chemical shifts of *n*-hexane and perfluoro-*n*-hexane in CO_2,[8] they observed a chemical shift in the C_6F_{14} spectra, which they ascribed to C_6F_{14}–CO_2 van der Waals interactions. By contrast, Yonker *et al.* showed (using ^{1}H and ^{19}F NMR) that

neither fluoromethane (CH_3F) nor trifluoromethane (CHF_3) exhibit significant specific attractive interactions with CO_2.[9]

Theoretical studies have also resulted in contradictory findings. Using restricted Hartree–Fock level *ab initio* calculations, Cece *et al.* suggested that there exist specific interactions between CO_2 and the fluorines of C_2F_6.[10] Han and Jeong,[11] however, disagreed with these results, noting that Cece *et al.* did not take into account basis set superposition error (BSSE) corrections during their calculations. Using similar *ab initio* calculations, but accounting for BSSE corrections, Diep *et al.*[12] reported no evidence of CO_2–F interactions in perfluorinated compounds. Raveendran and Wallen computationally investigated the effect of stepwise fluorination on the CO_2-philicity of methane in an effort to address the existence of F–CO_2 interactions. In partially fluorinated systems, the fluorine atom acts as a Lewis base towards electron deficient carbon atom of CO_2, and the hydrogen atoms, having increased positive charge due to the neighboring fluorine, act as Lewis acids towards the electron rich oxygen atoms of CO_2.[13]

Fried and Hu used MP2 calculations (6-31++G** basis set) in an effort to identify the nature of specific interactions between CO_2 and fluorinated substituent groups on polymers.[14] They reported that quadrupole–dipole interactions are important contributors to the total energy of interaction. In experimental studies by McHugh *et al.*, the favorable miscibility of fluorocarbons has also been attributed to polar–quadrupole interactions.[15] The authors noted that fluorination imparts solubility to the polymer provided that polarity is also introduced to the polymer *via* such fluorination. Too high a level of fluorination produces an adverse effect on miscibility due to dominance of dipole–dipole interactions between polymer chains.[16]

Clearly, there is considerable controversy in the literature surrounding the origin of the miscibility of some fluorinated polymers in CO_2, yet there do seem to be some interesting lessons to be learned from this work regarding CO_2-phile design, namely:

• The presence of fluorine creates molecules with weak self-interaction, rendering miscibility with CO_2 possible at lower pressures;

• Electronegative fluorine may exhibit specific interactions with CO_2's electron poor carbon, lowering miscibility pressures;

• The presence of fluorine will affect the acidity of neighboring protons, allowing for the possibility of specific interactions between these protons and CO_2's oxygen atoms.

Non-fluorous CO_2-philes: the role of oxygen

We have explored the possibility that one could design a non-fluorous CO_2-phile, basing our early designs on intriguing literature on interactions between oxygen-containing functional groups and CO_2. For example, Kazarian and coworkers reported the existence of Lewis acid–Lewis base interactions (*via* FT-IR) between CO_2 and the oxygen of a carbonyl.[17] In this and other studies, it was shown that the carbonyl oxygen interacts with the carbon atom of CO_2, where the geometry and strength of the interaction may vary depending on adjacent groups. The use of oxygen-containing functional groups appeared particularly advantageous in CO_2-phile design because it allows for creation of specific interactions with CO_2 while minimizing the strength of self-interactions of the solute.

We subsequently showed that addition of carbonyl-containing functional groups lowers the miscibility pressures of silicones[18,19] in CO_2; the combination of weak self-interaction (silicones) and CO_2:carbonyl group interaction is clearly favorable. Addition of ether groups to a silicone backbone also lowers miscibility pressures; our subsequent calculations suggested equal strength of interaction between ether oxygen:CO_2 and carbonyl oxygen:CO_2 pairs, allowing for strategic combinations. In Fig. 2a, we note that addition of an oxygen atom to the backbone of polypropylene (creating in effect polypropylene oxide) lowers miscibility pressures dramatically. Placing the oxygen in the side chain (Fig. 2b), and lengthening the chain (polyvinyl ethyl ether) depresses miscibility pressures further (likely here *via* enhanced free volume). In Fig. 2c, we see that addition of a carbonyl oxygen to polyvinyl ethyl ether (in effect creating polyvinyl acetate) lowers miscibility pressures again. The particular utility of acetates in lowering miscibility pressures in CO_2 was demonstrated by Wallen[20] and by our group[21] using acetate-functional saccharides and polysaccharides.

To our CO_2-phile molecular "wish list" of weak self-interaction and oxygen:CO_2 interactions we added high flexibility/low softening point, assuming that this characteristic would enhance the entropy of mixing of the compound with CO_2. We then designed a series of ether–carbonate copolymers that exhibited lower miscibility pressures than the fluorinated polyethers we had employed as CO_2-philes for over a decade.[22] Nevertheless, our set of guidelines remained simply guidelines; true *a priori* design was not possible. In
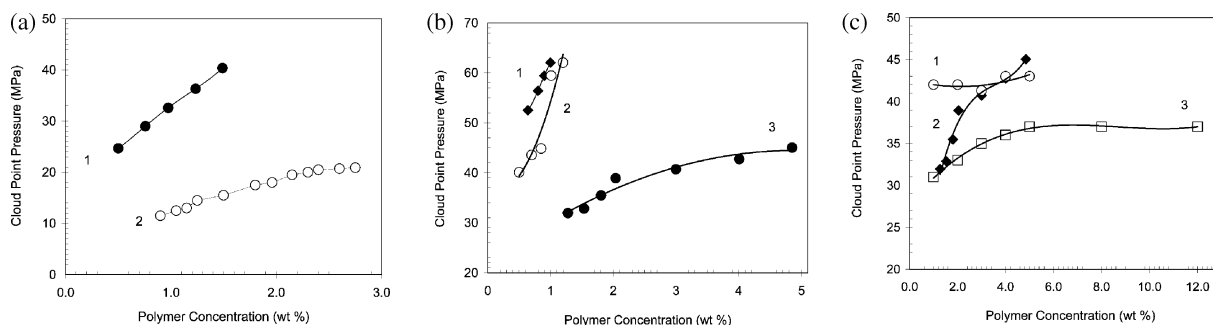
Fig. 2 (a) Phase behavior of (1) atactic polypropylene (Mw = 425), (2) poly(propylene glycol)-monomethylether (Mw = 1000), in carbon dioxide at 295 K. (b) Phase behavior of oxygen-containing polymers in carbon dioxide at 295 K (1) polypropylene glycol dimethyl ether, Mw = 3500, (2) poly(vinyl methyl ether), Mw = 3850, (3) poly(vinyl ethyl ether), Mw = 3800. (c) Phase behavior of oxygen-containing polymers in carbon dioxide at 295 K, (1) poly(vinyl acetate), Mw = 7700, (2) poly(vinyl ethyl ether), Mw = 3800, (3) poly(vinyl acetate), Mw = 3090.

particular, we noted that very small changes to structure led to dramatic and unpredictable changes in phase behavior, a frustrating situation. For example, it has been known for almost a decade[21] that polymethyl acrylate (PMA) and polyvinyl acetate (PVAc) exhibit miscibility pressures in CO_2 that differ by hundreds of bar—this result would not be predicted by any group contribution thermodynamic model currently in use without purely empirical adjustments. Indeed, the PMA/PVAc effect is preserved even when we attach the ester group in either an "acrylate" or "acetate" fashion to other polymer backbones (see Fig. 3). Finally, while polyvinyl acetate exhibits relatively accessible miscibility pressures (Fig. 2c), we have found that the addition of a single methylene unit (polyallyl acetate) creates a

material that is for all intents and purposes, insoluble. Again, traditional thermodynamic models provide no guidance here.

We believe that at least part of the answer to these puzzles lies in CO_2's ability to act as both Lewis acid and Lewis base, coupled with subtle effects of neighboring substituents on the acidity of certain protons. For example, Wallen and colleagues,[23] in an analysis of interactions between acetate groups and CO_2, found that the acidity of the methyl acetate protons allows for binding of CO_2 through both its carbon and oxygen atoms. We[24] have found experimentally that copolymers of vinyl acetate (VAc) and tetrafluoroethylene (TFE) exhibit lower miscibility pressures than either of the homopolymers. Not surprisingly, calculations made (using MP2/aug-cc-pVDZ level of theory) on the geometry and strength of the interactions between CO_2 and various dyads (TFE-VAc, VAc-VAc, *etc.*) in the copolymer showed that the presence of the difluoromethylene groups in the backbone render neighboring protons more acidic. This neighbor effect allows quadradentate binding between CO_2 and the TFE–VAc dyad (Fig. 4). Given our results with TFE–VAc copolymers, we are currently endeavoring to design a structure that might incorporate the benefits of this copolymer, yet without the need for fluorine.

In summary, combinations of theory and experiment are rapidly advancing our ability to design cost-effective CO_2-philic materials. We would propose the following molecular characteristics for a "CO_2-phile":

• Flexible, high free volume materials: Eastoe and colleagues[25] have previously demonstrated that increasing free volume through functional group changes will enhance solubility of compounds in CO_2. Elevating free volume and flexibility can,

Fig. 3 Phase behavior of two functionalized silicone polymers in carbon dioxide at 295 K, structures shown below.
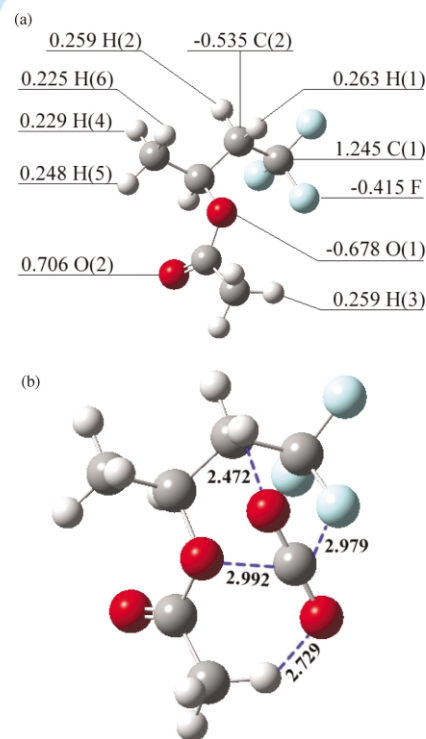

Fig. 4 (a) Charge distribution on model for TFE–VAc dyad calculated using Gaussian 98 package, revision A11; note charges on protons next to carbonyl and CF_3 group. (b) Optimized binding geometries for the CO_2 – TFE–VAc dyad using MP2/6-31+g(d) level of theory; optimized configurations were then used to calculate the more accurate single point binding energies using the aug-cc-pVDZ basis set with counterpoise corrections.
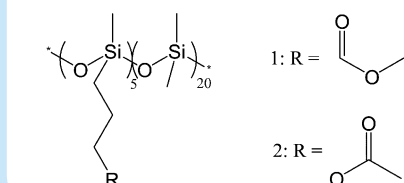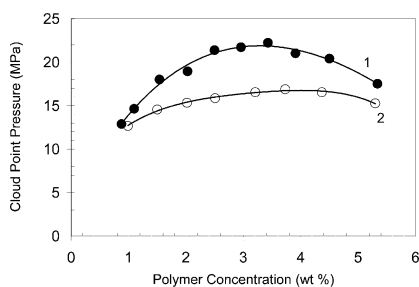
for example, be accomplished through branching and use of ether linkages in the main chain.

• Weak self-interactions. O'Neill and colleagues[26] previously noted that most of the CO_2-philes known exhibit relatively

weak self-interaction, as evidenced by low cohesive energy density. We have found, for example, that while tertiary amines interact more strongly with CO_2 than do carbonyls, the stronger self-interaction of the amine-containing compounds actually elevates their miscibility pressures in CO_2 *versus* oxygen-containing analogs.

• Multidentate interactions between CO_2 and solute functional groups, where interactions involve both the carbon and oxygens in CO_2. Oxygen-containing functional groups are advantageous in that they interact with CO_2, adjust the acidity of neighboring protons, and add comparatively little to the strength of self-interaction of the solute.

If one examines the structure of the most CO_2-philic material identified to date, the poly(perfluoroacrylate) shown in Fig. 1, one can see that it fortuitously incorporates all of the features described above. Poly(FOA)'s fluorinated side chain creates a flexible material with high free volume (evidenced by a low glass transition temperature) and relatively weak self-interactions. The fluorines provide possible sites for specific interactions with CO_2, *and* render neighboring protons relatively acidic, providing the potential for multi-dentate interactions. The carbonyl group and its neighboring acidic protons also provide such sites. In future, our task lies in creating a non-fluorous analog to Poly(FOA) using these design rules.

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