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Sugar Acetates as Novel, Renewable CO_2-philes

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Supercritical carbon dioxide ($scCO_2$) has attracted much attention as a "green" replacement for organic solvents,[1−3] offering economical and environmental benefits due to its favorable physical and chemical properties. Recyclability, ease of solvent removal, and readily tunable solvent parameters make $scCO_2$ a desirable alternative over conventional solvents. Among potential uses of $scCO_2$, synthesis and extraction of biologically important molecules as well as separation of natural products such as proteins and carbohydrates has immense importance. However, most biological compounds are polar and exhibit very low solubility in $scCO_2$, limiting the applications of $scCO_2$ in this area. Also of importance is the design and synthesis of CO_2-philic materials, which can be modified as surfactants for water-in-CO_2 and organic-in-CO_2 reverse microemulsions for use in the separation of CO_2-insoluble compounds by using minimal amounts of conventional solvents. Thus, recently there have been numerous theoretical and experimental approaches to CO_2-philize molecules. The most important method so far has been the incorporation of fluorocarbons due to their high miscibility with $scCO_2$. However, the use of fluorocarbons as CO_2-philes has met with several disadvantages due to their high cost and potential issues concerning degradation.

Most recently, hydrocarbons substituted with carbonyl groups have been proposed as economical, environmentally benign CO_2-philes. The high solubility of these carbonyl systems in $scCO_2$ was attributed to the Lewis acid (LA)−Lewis base (LB) interactions between CO_2 and CO_2-philic Lewis base functionalities such as carbonyl groups.[5−8] Ab initio calculations[7,8] indicate that the interaction between the carbonyl groups of an acetate functionality and CO_2 is almost half as strong as the hydrogen bond interaction in a water dimer. IR spectroscopic studies[6] have confirmed this view of specific interactions between CO_2 and the carbonyl groups. Based on these revelations, by optimizing the enthalpic and entropic factors, Beckman and co-workers synthesized poly(ether-carbonate) copolymers with relatively high solubility in $scCO_2$.[5] Our recent ab initio calculations have shown that in the case of carbonyl systems having hydrogen atoms attached to the carbonyl carbon or the α-carbon atom, as in the aldehyde or acetate groups, a weak, but cooperative C−H···O hydrogen bond involving these types of hydrogens and one of the oxygen atoms of CO_2 reinforces the LA−LB interactions.[8] The cooperativity of these two interactions is illustrated in Figure 1.

Ab initio calculations[8] on simple carbonyl systems revealed that methyl acetate has the strongest interaction with CO_2 (2.82 kcal/mol at the MP2/aug-cc-pVDZ level) suggesting that the acetylation of hydroxyl groups might be a viable approach to CO_2-philize hydroxylated compounds, thereby increasing their solubility. The abundance of hydroxyl groups in carbohydrates, which are renewable compounds, opens a wide range of possibilities for the synthesis of CO_2-philes at reasonable cost.

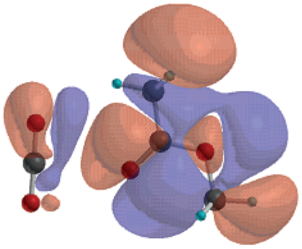

Figure 1. The highest occupied molecular orbital (HOMO) for the optimized geometry of the CO_2−methyl acetate complex calculated at the MP2/6-31+G* level. The C−H···O hydrogen bond acts cooperatively with the Lewis acid−Lewis base interaction (CO_2−carbonyl) introducing further stabilization.

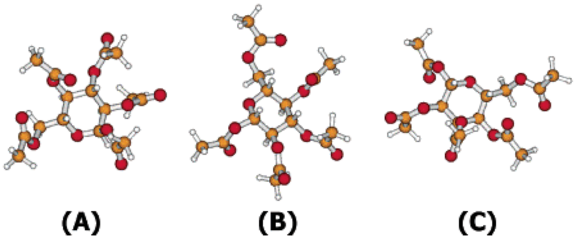

Figure 2. Optimized structures of (A) AGLU, (B) BGLU, and (C) BGAL.

Guided by these principles, we selected three carbohydrate derivatives as model systems for our studies: the α- and β-forms of 1,2,3,4,6-pentaacetyl-D-glucose (AGLU and BGLU, respectively) and 1,2,3,4,6-pentaacetyl β-D-galactose (BGAL). The geometries of these molecules optimized by using density functional theory (DFT) with the B3LYP functional and 6-31+G* basis set are given in Figure 2.

BGLU is a white solid that melts at 132 °C under atmospheric pressure conditions (Figure 3A). However, as BGLU is exposed to CO_2 near room temperature (23.0 °C) in a conventional high-pressure view cell, it absorbs CO_2 and becomes "wetted" with CO_2 at a pressure of 35−40 bar. The white solid appears as a salt does in a humid environment. Furthermore, at a gaseous CO_2 pressure of 55.9 bar a solid-to-liquid transition (deliquescence) occurs (Figure 3B). This is analogous to the deliquescence of hygroscopic materials absorbing atmospheric moisture. The carbohydrate melt continues to absorb CO_2 and swells to many times its original volume with changes in the gaseous CO_2 pressure of only 2 and 3 bar as illustrated in Figure 3, panels C and D, respectively. Upon reaching the liquid−vapor equilibrium pressure, the liquid CO_2 forms a separate layer on top of the viscous melt containing CO_2. However, the melt easily mixes with the upper layer of liquid CO_2 on stirring and forms a single-phase liquid mixture in contact with the gaseous CO_2 phase (Figure 3E). Further addition of CO_2 only dilutes this

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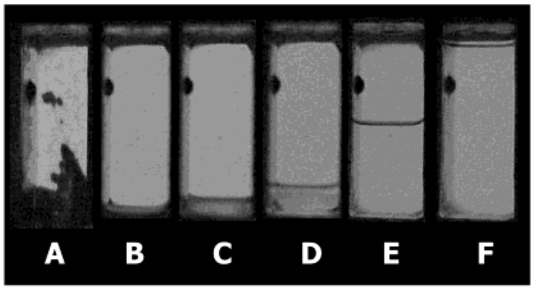

Figure 3. Photographs showing the deliquescence, swelling, and dissolution of BGLU in CO_2 at 23.0 °C: (A) solid material; (B) at the deliquescence pressure (55.9 bar) with a gaseous CO_2 phase in contact with the viscous liquid BGLU forming the lower phase; (C) swelling of the BGLU liquid phase with an increase of CO_2 pressure (57.9 bar); (D) continued swelling of the BGLU liquid phase with an increase of CO_2 pressure (58.9 bar); (E) the melt phase at the CO_2 liquid−vapor equilibrium pressure (60.5 bar) and after stirring; (F) complete miscibility of the melt in liquid CO_2 with additional CO_2 (60.5 bar).

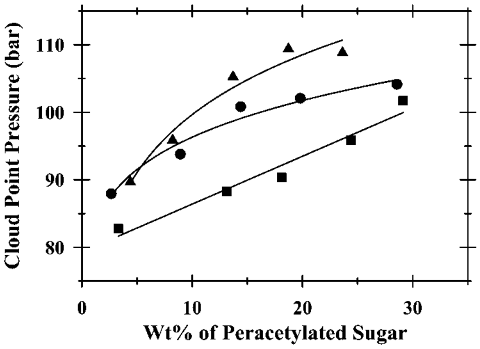

Figure 4. Plots of the cloud-point pressure versus the weight percentage of the carbohydrate derivative for AGLU (■), BGLU (●), and BGAL (▲) in supercritical CO_2 at a temperature of 40.0 °C.

liquid phase (Figure 3F). Although, CO_2-induced swelling[9] and CO_2-assisted melting point depression[10] have been reported in polymers by sorption of CO_2 under high pressures, the materials are not readily miscible in liquid and supercritical CO_2, indicating the lack of a significant attractive interaction.

The deliquescence of BGLU on CO_2 sorption and their mutual miscibility reveal a strong affinity between CO_2 and BGLU, indicating a unique solute−solvent interaction cross-section assisting the formation of solvation shells around the solute molecule.

An approximate estimate of the BGLU concentration in the melt reveals that the system contains more than 80 wt % of BGLU and can be diluted with liquid or $scCO_2$ in any proportion desired. This suggests that this system or larger derivatives may be used for tuning the viscosity of liquid and supercritical CO_2 solutions as desired at low pressures and elevated temperatures. The deliquescence point of AGLU is lower than that of BGLU by about 6−7 bar. BGAL does not exhibit deliquescence though it is readily soluble in liquid CO_2. These observations can be directly correlated to the differences in lattice energies as reflected in the melting points of AGLU, BGLU, and BGAL (109, 132, and 142 °C, respectively). Our preliminary density functional calculations suggest a large number of intramolecular C−H···O interactions (Figure 2) that may play a crucial role in determining the lattice energy by lessening intermolecular contacts. This can also effectively reduce the CO_2-specific interaction cross-section, which should be reflected in the solubility of the three carbohydrates.

The cloud-point pressures of these systems in $scCO_2$ were examined at 40.0 °C. As in the subcritical case, initially the solid melts and swells (for AGLU and BGLU) and all three peracetylated sugars readily go into a single-phase, $scCO_2$ system. A plot of the cloud-point pressure versus the weight percent for AGLU, BGLU, and BGAL dissolved in supercritical CO_2 at 40.0 °C is given in Figure 4. At the cloud-point pressure, phase separation begins between $scCO_2$ and the sugar ester. Upon lowering the pressure, the material reappears in the solid state. No cloud-point measurements were made above 30 wt % due to limitations arising from the volume of the view cell and the rapid swelling of the sample in the cases of AGLU and BGLU. Considering this cloud-point data and the data presented in Figure 3, it is apparent that the mixtures of AGLU and BGLU show complete miscibility at relatively low pressures with the 3-phase line being shifted to extremely low pressures. An understanding of the stereochemical aspects revealed here may provide important insight toward the design of larger CO_2-philic molecules since there is a definite dependence on the configuration of the individual isomers.

In summary, we have presented the deliquescence of peracetylated sugars in contact with gaseous CO_2 and their unparalleled solubility in liquid and $scCO_2$. The dissolution of these biomaterials in $scCO_2$ indicates that these compounds may be readily modified as ionic or nonionic surfactants for the formation of water-in-CO_2 or organic-in-CO_2 reverse microemulsions by attaching hydrophilic or hydrophobic ends, respectively. This represents the first example of renewable, biologically derived, nonvolatile materials with high miscibility (AGLU and BGLU) and solubility (BGLA) in neat CO_2. The fact that peracetylated sugars serve as intermediates in a wide range of carbohydrate chemistries suggests that liquid and $scCO_2$ could serve as a unique solvent for reactions as well as analytical and preparative separations in carbohydrate chemistry.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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