Polar Attributes of Supercritical Carbon Dioxide

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ABSTRACT

Supercritical carbon dioxide ($scCO_2$) is increasingly promoted as an environmentally benign alternative to conventional organic solvents. The supercritical state bridges the gap between liquid and gaseous states by offering gaslike diffusion rates and liquidlike solvent densities, thereby enabling potential opportunities as a reaction and separation medium in chemical industry. Understanding the solvent behavior of liquid and $scCO_2$ is of critical importance to enable the design of CO_2-philic molecular systems and to expand the use of these solvent systems to a wider range of chemical processes. Historically CO_2 was treated as a nonpolar solvent, primarily because of its low dielectric constant and zero molecular dipole moment. CO_2 has also been described as a quadrupolar solvent because of its significant quadrupole moment. Recent studies suggest that, as far as the microscopic solvent behavior of CO_2 is concerned, CO_2 has the potential to act as both a weak Lewis acid and Lewis base. Also, strong theoretical and experimental evidence indicates that CO_2 can participate in conventional or nonconventional hydrogen-bonding interactions. All of these site-specific solute−solvent interactions are important to understand the fundamental nature of CO_2 as a solvent. In this Account, we discuss these *polar* attributes of CO_2 and their relation to solvation.

Introduction

Although $scCO_2$ has received much attention within academic and chemical industrial laboratories both as a *green* alternative to conventional organic solvents and as a simple, linear triatomic molecular system, the solvent behavior of CO_2 is not well-understood on a microscopic level. The nontoxicity, low cost, abundance, and ease of recycling are some of the key attributes of this environmentally benign solvent.[1−14] The low critical temperature of CO_2 (T_c = 31.1 °C) ensures that $scCO_2$ is a safe solvent for biomolecular separations, pharmaceutical applications, and in other thermally labile systems.[7] CO_2 is a major byproduct in several industrial processes, and in terms of availability, it is almost as readily abundant as H_2O. Additionally, because CO_2 is recognized as a "green house" gas, recycling of byproduct gas and its industrial utilization are an important mode of reducing emissions into the atmosphere. Over the past 2 decades, there are several areas where CO_2 research has progressed with developments in applications such as CO_2-based dry cleaning, polymer synthesis,[1] extraction and separation of natural products,[3] chemical transformations,[8−11] synthesis and dispersion of nanoparticles,[12,13] and materials processing.[14] However, the large-scale utilization of this solvent suffers from the lack of a molecular level understanding of the solvation phenomenon in CO_2. How is CO_2 classified as a solvent? What are the basic characteristics concerning solvation in CO_2, and how is it different from common solvents such as hexane and H_2O? What sort of molecular systems can CO_2 dissolve, and what types of interactions predominate? These are some of the important issues that need to be addressed before it is possible to expand the use of CO_2 as an industrial solvent.

Successful liquid-state models incorporating the large amplitude charge separation and opposed pair of bond dipoles in CO_2 (quadrupole) are well-known among researchers focused on the liquid state. However, in general, initial efforts to describe the solvent properties of $scCO_2$ considered it as a nonpolar solvent. In fact, CO_2 also has a low molecular polarizability compared to alkanes, and some scientists even tend to describe CO_2 as a solvent extremely contrasting H_2O. The dielectric constant of liquid or $scCO_2$ is even lower than that of

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hydrocarbons, and therefore, initially, it was widely perceived that CO_2 should be an alternative for hydrocarbon solvents. This view, however, did not last long with Consani and Smith, showing that many of the molecular systems possessing hydrocarbon chains are not highly soluble in CO_2.[15] An established class of compounds that are highly miscible with $scCO_2$ is the fluorocarbons, and there are several conflicting views about their "preferred" solvation in CO_2.[16−21] Some of the more recent additions to the list of CO_2-philic materials are carbonyl-containing molecular systems such as poly(ether-carbonate) copolymers[22] and sugar acetates.[23] These facts along with recent computational[21,24−26] and spectroscopic studies[27−33] suggest a rather polar nature of $scCO_2$ as a solvent.

A rule of thumb that chemists first learn regarding solvation is that "like dissolves like". In general, while polar solvents dissolve polar and ionic solutes, nonpolar solvents dissolve nonpolar solutes. Thus, if we are able to develop a basic understanding about the molecular attributes of CO_2, it will help to identify the general types of molecular systems that are solvated by CO_2. Also, these CO_2-philes will potentially serve as CO_2-philic molecular fragments, which can be used to solubilize otherwise insoluble molecular systems. The question to be addressed is whether the low dielectric constant and zero dipole moment of CO_2 do indeed represent its solvent behavior accurately, especially considering that the former is mostly a direct consequence of the latter.

Nondipolar Solvents

A great volume of literature is available on the energetics of solvation in dipolar solvents using experimental and theoretical methods. Most of the experimental work is based on electronic and vibrational spectroscopic studies aimed at monitoring frequency shifts experienced by probe molecules as a result of solvation. Generally, in these studies, the solvent polarity is described by the value of the dielectric constant, ϵ.[33] Although the dielectric continuum models explain the solvatochromic effects in most cases reported, there are several instances where it fails to explain the solvent behavior well because these models often do not fully account for the microscopic solvation characteristics around the solute. This is particularly important when there are significant site-specific, solute−solvent interactions involved.

Computational approaches, especially higher level quantum chemical calculations, provide excellent insight into understanding the microscopic solute−solvent interactions. However, such accurate computational models are limited with respect to condensed phase systems, although detailed *ab initio* molecular dynamics methods are being developed. In some systems, even if the solvent molecule has a zero dipole moment as a result of molecular symmetry (and correspondingly low ϵ), there are significant bond dipoles and consequent multipole (quadrupole, octapole, ...) moments present as a result of the static charges on the individual atoms. For example, benzene has a zero dipole moment and a low dielectric constant but has a considerable quadrupole moment. This leads to solvation processes aided by quadrupole−dipole interactions and quadrupole-induced dipole interactions. Such systems are generally described as nondipolar solvents, indicating that these are still polar in nature because they may dissolve dipolar or nondipolar solutes. Several research groups have carried out extensive studies to address this issue.

For instance, Maroncelli and co-workers[33] tried to correlate the solute−solvent microscopic interactions and the predictions from the continuum dielectric models, for a range of solvents, by measuring the Stokes shifts associated with the steady-state and time-resolved emission spectra of a dissolved solvatochromic probe. One notable anomaly that highlights the inadequacy of dielectric continuum models is dioxane. Despite its low dielectric constant and dipole moment ($\mu = 0.45$ D), the Stokes shifts observed in 1,4-dioxane are comparable to those of tetrahydrofuran (THF, $\mu = 1.75$ D). Continuum dielectric constants, however, predict a very low reaction field factor for dioxane compared to THF. The low dipole moment of dioxane is a result of the cancellation of the symmetrically arranged bond dipoles, while the observed solvation energetics are a result of the similar local bond polarities of THF and dioxane. In the case of CO_2, there is also a considerable Stokes shift comparable to that of benzene and hexafluorobenzene.[33] While multipole moments explain the solvation energetics of nondipolar solvents to some extent, it is obvious that symmetrically arranged charges in molecules can lead to the cancellation of multipole moments while the solvent is still effective at dissolving certain solutes.[33] Therefore, it is necessary that any discussion of the solvation dynamics and energetics in nondipolar solvents should address the electronic charge separation on individual atoms and the resulting bond dipoles.

Solvent Attributes of CO_2

CO_2 is an excellent example of a simple, nondipolar solvent system. Although CO_2 has a zero dipole moment, it is a charge-separated molecule with significant nonzero bond dipole moments. This charge separation results in a significant quadrupole moment, and CO_2 is described as a quadrupolar solvent.[33,34] The behavior of CO_2 is similar to dioxane. However, one needs to address whether the quadrupolar description is sufficient to describe the site-specific, microscopic solvent characteristics of CO_2. A more "chemical" description has evolved recently regarding the solvation behavior of CO_2, which can act as a weak Lewis acid (LA) as well as a Lewis base (LB). One needs to examine the solvent attributes of CO_2 from this perspective. This view suggests that CO_2 can solubilize several dipolar and nondipolar molecular systems facilitated by site-specific solute−solvent interactions.

One classic example illustrating the polar nature of CO_2 is its higher solubility in H_2O compared to that of carbon monoxide (CO). Solubility is a thermodynamic indicator for the solute−solvent correlation in solution. When the

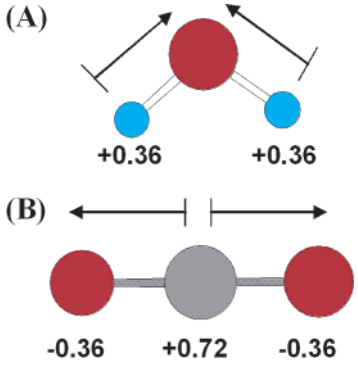

FIGURE 1. Bond dipoles and the atomic charges (CHELPG) on individual atoms of (A) H_2O and (B) CO_2.[21]

solute is a gas (i.e., CO or CO_2), its Ostwald absorption coefficient is directly related to the excess chemical potential of the solute in solution. It is generally accepted that the excess chemical potential is more positive (i.e., repulsive) when the solute size is larger and more negative (i.e., attractive) when the solute−solvent interaction is stronger. Because CO is smaller in size than CO_2 and possesses a net dipole moment, one would assume that CO should be more soluble in H_2O. The higher solubility of CO_2 in H_2O can be attributed to a stronger solute−solvent interaction, despite its zero dipole moment. Evidence of this comes from molecular dynamics studies by Sato et al.,[24] which identified a hydrogen bond between an oxygen in CO_2 and a hydrogen in H_2O. Such hydrogen bonds were not observed in the CO−H_2O system, indicating that site-specific, solute−solvent interactions are more important in the solvation of CO_2 by H_2O. These studies also revealed considerable interaction between the carbon of CO_2 and the oxygen in H_2O. Additionally, CO_2 is a well-known acid gas that forms weak carbonic acid when dissolved in H_2O.

Comparison between CO_2 and H_2O

Dipole−quadrupole interactions with solute molecules are considered to be responsible for many of the polar attributes of CO_2. For example, Kauffman's group demonstrated that this type of interaction is responsible for the local density augmentation observed under near-critical conditions.[34] Their study attributes the solvation behavior of CO_2 to its large quadrupole moment. This charge separation with partial negative charges on the electronegative oxygens, considerable partial positive charge on carbon, and the overall electronic structure suggests that CO_2 can act as either a weak Lewis acid or Lewis base. This is analogous to the situation in H_2O, although not as effective. In a recent work, Raveendran and Wallen[21] compared the charges on the individual atoms in CO_2 and H_2O as presented in Figure 1.

The charge separations in CO_2 and H_2O are quite comparable. This suggests the potential for significant site-specific interactions between solute molecules and CO_2 that are reminiscent of the enhanced dissolution of CO_2 in H_2O. However, the cooperative hydrogen-bond networks make H_2O a unique solvent for polar materials

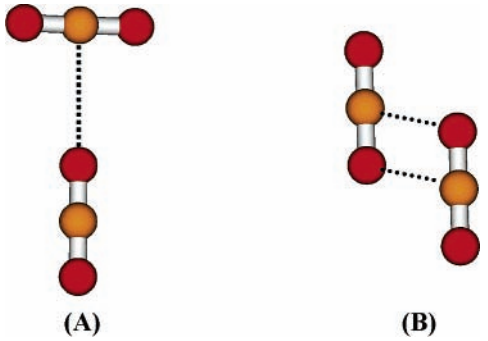

FIGURE 2. Optimized geometries of the (A) T-shaped and (B) slipped parallel configurations of the CO_2 dimer.[26,36]

unlike CO_2. Nevertheless, the results indicate that one should regard CO_2 as a polar molecule with two active and considerably strong bond dipoles. While the vectorial sum of these dipoles add to zero, the zero sum is not relevant to understanding CO_2 solvation from the microscopic point of view.

Self-Association of CO_2

Although the self-association of H_2O molecules has been a topic of extensive research over the past few decades using both spectroscopic and computational methods, such studies on CO_2 are limited. The investigations on gas-phase H_2O clusters clearly reveal the unique role of hydrogen bonding and the importance of the cooperative three-body interactions in the condensation of H_2O molecules as well as their role in solvating highly polar molecules and ions.[35] However, detailed investigations on the interaction between CO_2 molecules have so far been limited to its dimer and trimer. Early spectroscopic studies were mainly concerned with the structure of the CO_2 dimer. Although the initial gas-phase studies suggested a T-shaped dimer (C_{2v}), corresponding to a purely quadrupolar interaction, later molecular-beam diffraction studies by Miller and co-workers demonstrated that, in fact, the CO_2 dimer has a slipped parallel structure (C_{2h}) as shown in Figure 2.[36]

Studies of the CO_2 trimer are also important because the trimeric structure provides insight into the three-body effects in larger CO_2 clusters as well as in liquid or $scCO_2$. Wedia and Nesbitt reported two trimer structures based on IR spectral studies of supersonic jet expansions.[37] One of these is a cyclic structure (C_3), while the other is noncyclic (C_2), with the cyclic trimer being more abundant than the noncyclic trimer. After this, Tsuzuki et al. calculated the interaction energies for both of these structures using high-level *ab initio* methods and demonstrated that the noncyclic structure is slightly more thermodynamically stable (~0.38 kJ/mol) than the cyclic structure.[38] These researchers also calculated (MP2 level) the effects of three-body interactions in both systems and observed a small but attractive (cooperative) three-body term for the cyclic structure, while the three-body term is repulsive for the noncyclic structure. However, for both systems the three-body term is negative (attractive) at the Hartree−Fock level, but the contribution from electron

correlation is repulsive. Tsuzuki et al. concluded that the differences between the three-body terms are largely due to the differences at the HF level and thus a result of induction energy.[38]

Interaction of CO_2 with Lewis Bases

It is well-established that the electron-deficient carbon atom of CO_2 can act as a Lewis acid (LA) and participate in stabilizing interactions with Lewis base (LB) groups. Using IR spectroscopy, Kazarian et al. reported that carbonyl groups can participate in such LA−LB interactions with CO_2.[27] In this study, the degeneracy of the bending vibrational modes (ν_2) of CO_2 was lifted upon binding to carbonyl groups. On the basis of spectroscopic studies, Meredith et al. calculated the equilibrium constants for several LA−LB complexes of CO_2, establishing the rather "chemical" nature of these interactions.[28] Nelson and Borkman investigated the splitting of the degenerate ν_2 bending modes of CO_2 using *ab initio* calculations.[25] It is believed that these interactions play a pivotal role in the solvation of such materials and can be utilized for the design of CO_2-soluble materials.[22] Raveendran and Wallen also investigated the interaction between CO_2 and several model carbonyl compounds using *ab initio* molecular orbital calculations.[26] On the basis of these calculations, acetylation of polyhydroxyl systems was suggested as a simple route to synthesize highly CO_2-soluble compounds.[23,26]

Hydrogen Bonding with CO_2

Previous sections of this paper indicate that, by virtue of charge separation, the oxygen atoms of CO_2 molecules may participate in attractive interactions with Lewis acids (or electron-deficient molecular systems) and thereby enhance the solvation of these compounds in liquid and $scCO_2$. It is also important to investigate whether the CO_2 oxygen atoms can participate in hydrogen bonding with molecular systems carrying electron-deficient hydrogen atoms. Raveendran and Wallen's *ab initio* calculations on binary complexes of CO_2 with model carbonyl compounds, such as acetaldehyde and methyl acetate, also revealed that, indeed, the CO_2 oxygen participates in a cooperative C−H···O hydrogen bond (Figure 3A) with the electron-deficient hydrogen atoms that are attached to the carbonyl carbon atoms or to the α-carbon atoms.[26] The calculated HOMO (highest occupied molecular orbital) of the methyl acetate−CO_2 complex (Figure 3B) also suggests the formation of the C−H···O hydrogen bonds.[23]

Further evidence supporting the formation of a weak, cooperative, hydrogen bond is obtained by careful examination of the optimized geometries of the CO_2 complexes with the model carbonyl compounds. These indicate that the C−O bond of CO_2 involved in the C−H···O hydrogen bond is longer than the "free" one.[26] Additionally, the calculated charges on the individual atoms support the formation of a C−H···O hydrogen bond between CO_2 and the model carbonyl compounds.[26] Raman spectroscopic studies of room-temperature gaseous mixtures of acetaldehyde and CO_2 mixtures provided experimental evidence for the presence of both the LA−LB interaction (Figure 4A) between CO_2 and the carbonyl group as well as a weak, blue-shifting, C−H···O hydrogen bond (Figure 4B).[29] The Raman band corresponding to the carbonyl stretching band red-shifts by 2.5 cm^{-1}, while the aldehyde C−H stretching band blue-shifts by 1.3 cm^{-1} on complexation with CO_2. The blue shift in the latter band is attributed to the cooperative C−H···O hydrogen bond between the aldehyde C−H and the CO_2 oxygen. Although low-temperature cluster spectroscopic methods are a better tool for correlations between experiment and theory, the room-temperature results shown in Figure 4 do provide the first experimental evidence explaining the proposed solvation mechanism of these solutes in CO_2. Additional NMR, IR, and Raman spectroscopic studies of the interaction between several model carbonyl systems and CO_2 also supported the formation of weak C−H···O hydrogen bonds with CO_2.[32]

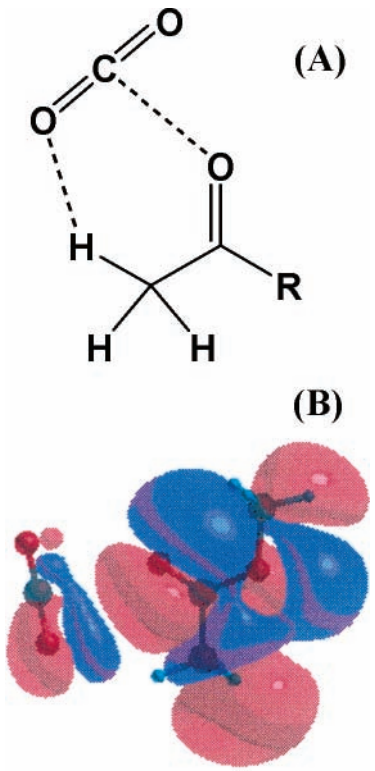

FIGURE 3. (A) Schematic representation of the LA−LB interaction between the carbonyl oxygen atom and the carbon atom of CO_2 and the cooperative C−H···O hydrogen bonding between the CO_2 oxygen and the $C_\alpha H$ bond. (B) Highest occupied molecular orbital for the optimized geometry of the methyl acetate−CO_2 complex.[23,26]

Experimental investigations also reveal the formation of conventional hydrogen bonds between an oxygen atom of CO_2 and hydroxyl (−OH) groups. For example, Fujii et al. reported the direct observation of a weak, conventional hydrogen bond between CO_2 and the −OH group of phenol in the mixed low-temperature, molecular clusters of phenol with CO_2 using IR spectroscopy.[30] The stretching vibration of the phenol −OH group red-shifts by 26 cm^{-1} on complexation with CO_2 (Figure 5). Although much weaker compared to the red shift observed for the −OH

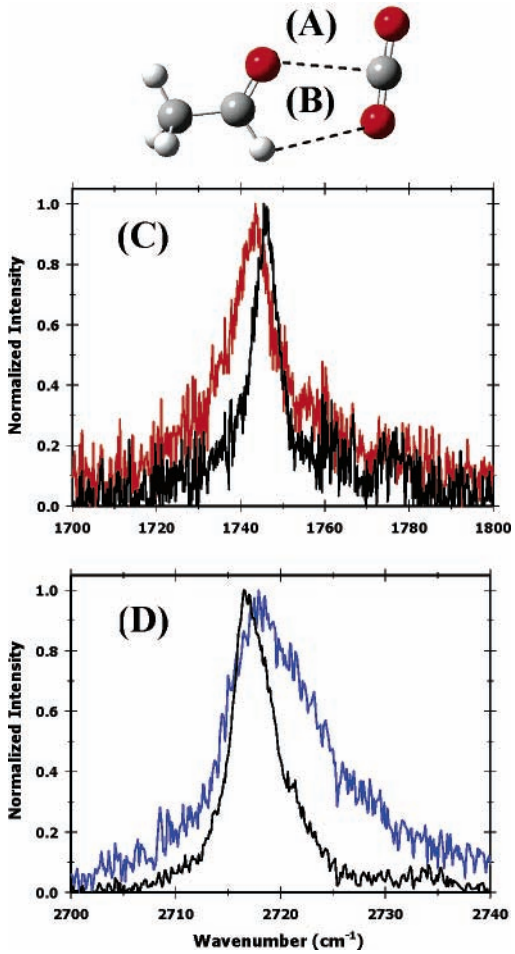

FIGURE 4. Spectroscopic evidence for the (A) Lewis acid−Lewis base and (B) C−H···O interactions. Raman spectra of acetaldehyde in (C) the carbonyl stretching region in pressurized He (black line) and CO_2 (red line) and (D) the aldehydic C−H stretching region in pressurized He (black line) and CO_2 (blue line).[29]

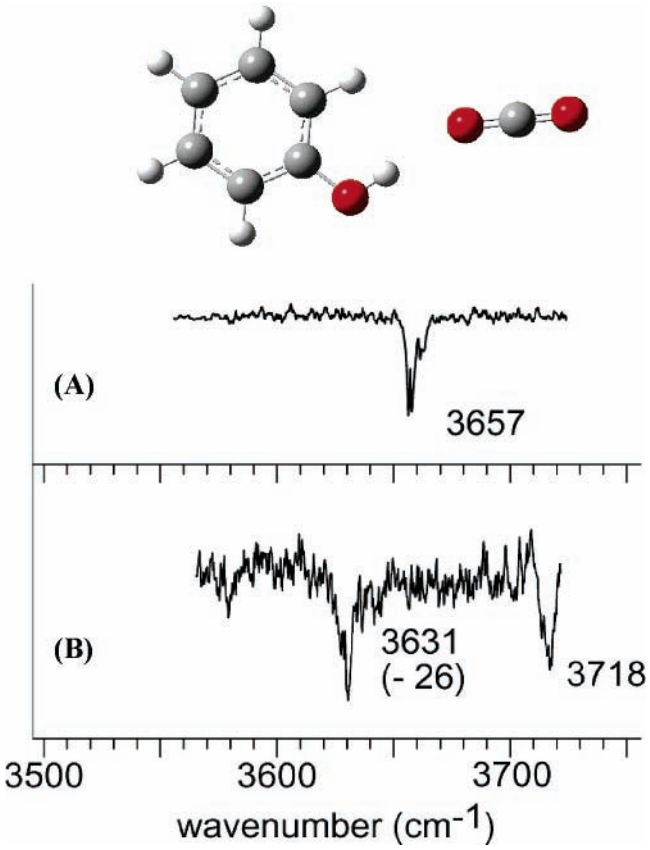

FIGURE 5. The O−H stretching region of the IR spectra of (A) bare phenol and (B) phenol−CO_2 in the neutral ground state (S_0). The optimized geometry is also given.[30]

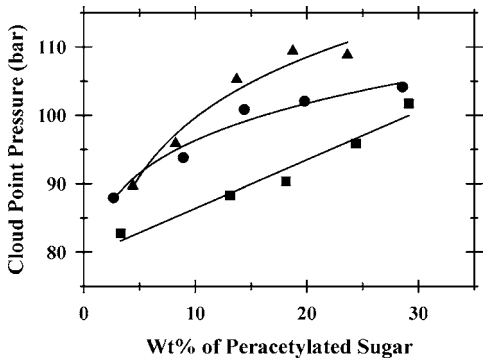

FIGURE 6. Plots of the cloud-point pressure versus the weight percentage of the peracetylated sugars in scCO$_2$ at a temperature of 40.0 °C: α-GLC (■), β-GLC (●), and β-GAL (▲).[23]

stretch of the H_2O dimer relative to monomeric H_2O, these results are significant. Other molecular systems such as CF_3H are also reported to form a hydrogen bond with CO_2.[21,31] IR spectroscopic studies of CF_3H dissolved in liquid CO_2 show a blue shift of the C−H stretching frequency compared to the noninteracting argon system.[31]

Hampe and Rudkevich report that CO_2 has the ability to form complexes with amine compounds with drastic changes in their fluorescence quantum yield.[39] Recent spectroscopic and computational studies on the effect that CO_2 has on the dimerization of carboxylic acids by Roberts and co-workers also support the view that CO_2 can form conventional hydrogen bonds, thereby, assisting the solvation of molecules.[40]

Solubility of Sugar Acetates in CO_2

Many biologically derived materials are highly polar and thus exhibit very low solubility in liquid and scCO$_2$. Recently, it was suggested that acetylation of polyhydroxyl systems such as carbohydrates may be used as an excellent method for making these systems highly CO_2-philic.[23] Raveendran and Wallen reported an anomalous solubility for sugar acetates in liquid and scCO$_2$. It was shown that pentaacetyl β-D-glucose (β-GLC, melting point = 132 °C) undergoes a process analogous to aqueous deliquescence in gaseous CO_2 around 55.9 bar at 23 °C. These CO_2-β-GLC gels absorb more CO_2 at higher pressures and swell to many times their original volumes. This system is also completely miscible with liquid and scCO$_2$. The cloud points of peracetylated glucose (α and β) and β-D-galactose (β-GAL) are given in Figure 6.

These results are important for several reasons. First, they show that a relatively polar class of materials such as the sugar acetates can be highly soluble in scCO$_2$, in contrast to the conventional view of the solvent behavior

of CO_2. This lends credence to the polar nature of CO_2 as a solvent. It also suggests an inexpensive and environmentally benign route aimed toward designing CO_2-soluble materials. In addition, the high solubility of the peracetylated sugars points toward the utilization of $scCO_2$ as a promising solvent for separations and reactions involving carbohydrate moieties in a wide range of molecular systems.

CO_2 Interactions with other Lewis Bases

In general, sp^3 oxygen atoms are better electron donors than sp^2 oxygen atoms. Therefore, ether and alcohol oxygen atoms are also expected to participate in LA−LB interactions with CO_2 similar to the carbonyl groups. Investigations by Besnard and co-workers[41] and van der Veken and co-workers[42] show that the interaction between CO_2 and the sp^3 oxygen of methanol or dimethyl ether is energetically almost as favorable as the carbonyl-containing functionalities discussed previously. The ester groups have an ether oxygen in addition to the carbonyl group, and these also substantially contribute to the solute−solvent interactions in a cumulative manner. Recent results from Beckman, Enick, and co-workers also support this view.[43] Additionally, it was recently reported by Heldebrant and Jessop that small molecular analogues of poly(ethylene glycol) are also soluble in $scCO_2$, suggesting that the ether−CO_2 interactions result in an enthalpy-driven solvation in liquid and $scCO_2$.[11] This also explains to some extent the solubility of the poly(ether-carbonate) copolymers in liquid CO_2.[22] Similar interactions are responsible for solvation in systems where Wai and co-workers utilized a scheme in which a CO_2-philic Lewis base (tri-*n*-butyl phosphate) acts as a carrier to disperse a CO_2-insoluble Lewis acid (HNO_3) in $scCO_2$ phase enabling dissolution of an ionic system (uranium dioxide).[44] This dissolution is most likely based on the formation of a Lewis acid−Lewis base complex, allowing a simple way to dissolve previously insoluble hydrophilic acids and other materials in $scCO_2$.

These studies and those previously discussed highlight the importance of addressing fundamental aspects in the design of CO_2-soluble materials, especially consideration of factors such as the enthalpic and entropic contributions from the solute−solute and the solvent−solvent interactions. The solubility of materials in CO_2 ultimately depends on how easily the solute−solute interaction energies can be overcome by the solute−solvent interaction energies.

CO_2−Fluorocarbon Interactions

The high solubility of perfluorinated systems relative to hydrocarbon analogues in CO_2 has attracted considerable interest from both academic and industrial laboratories. From an industrial standpoint, it enables the utilization of CO_2 as a "green" solvent for synthesis and other applications.[1] Several researchers have utilized fluorocarbon tails in the design of surfactants for the CO_2−H_2O interface with goals of preparing H_2O-in-CO_2 reverse microemulsions.[6] This allows solubilization of polar molecules in CO_2. Researchers have also adopted geometrically favored hydrocarbon structures in surfactant design.[45] In the latter case, however, the CO_2 pressures employed are much higher compared to the fluorocarbon-based systems.

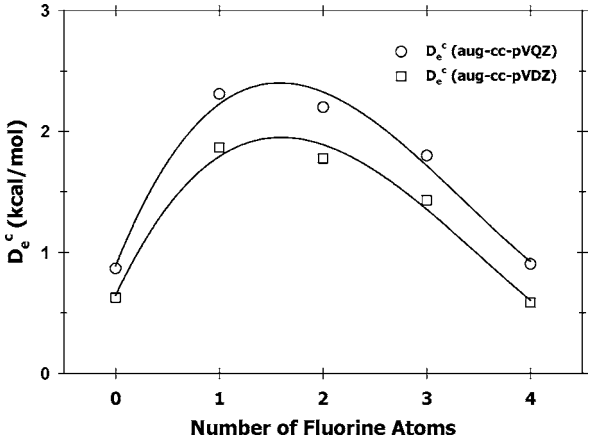

FIGURE 7. Variation of the dissociation energies (D_e^c) of the complexes of CO_2 with fluoromethanes versus the number of fluorine atoms (varying from 0 to 4), at the MP2 level using the aug-cc-pVDZ and the aug-cc-pVQZ basis sets.[21]

From an academic standpoint, several researchers have tried to understand the factors responsible for the high solubility of perfluorocarbons in $scCO_2$. Some groups suggest that the high miscibility of fluorocarbons with $scCO_2$ is a result of specific CO_2−fluorine interactions. On the basis of evidence from density-dependent ^1H and ^{19}F NMR studies of fluorocarbons and hydrocarbons in $scCO_2$, Dardin et al. postulated that there are specific solute−solvent interactions between CO_2 and fluorocarbons, while these are absent in the case of the corresponding hydrocarbons.[16] They hypothesized that these interactions resulted in enhanced dissolution of the former in CO_2. Several other experimental and theoretical studies, however, disputed this hypothesis and suggested that there are no such CO_2−fluorocarbon-specific interactions in comparison with the hydrocarbon systems.[17−20]

For clarification of this issue, Raveendran and Wallen recently carried out *ab initio* calculations on the interaction of CO_2 with fluoromethanes using a stepwise increase in the number of fluorine atoms.[21] Because fluorine atoms are highly electronegative, the initial fluorinations resulted in highly polar C−F bonds. However, further fluorine substitution results in competition among the individual electron-withdrawing fluorine atoms, thereby, making them weaker electron donors. After the interaction energies for the CO_2 complexes of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 were studied, it was determined that the interactions of CO_2 with CH_4 and CF_4 are energetically comparable while being fundamentally different. Additionally, the polar fluoromethanes interact more strongly with CO_2 than CF_4, and there is a turnover in the interaction energies as a function of the number of substituted fluorine atoms (Figure 7). These calculations also revealed that in partially fluorinated hydrocarbons, the C−H bonds, by virtue of their electron-deficient nature can participate

in C−H···O hydrogen bonds with the CO_2 oxygen atoms. One of the key aspects revealed from these studies is that the more polar fluoromethanes interact more favorably with CO_2 as compared to the less polar ones, irrespective of the fluorine number. This once again emphasizes the need to consider CO_2 as a polar solvent. However, it should be noted that the solubility of a material cannot be directly related to the pairwise interaction energies alone but also depends on the solute−solute, solute−solvent, and solvent−solvent interactions. Pairwise interaction energies do provide an understanding of the nature of the solute−solvent interactions that must be considered. The work cited here does help to clarify the differences in the hydrocarbon and perfluorocarbon interactions with CO_2; however, the mechanism for enhanced solubility of the latter is an open question.

Concluding Remarks

Understanding the solvent attributes of CO_2 is of tremendous importance in the prediction and design of CO_2-soluble materials as well as in expanding the utilization of $scCO_2$ as a "green" solvent alternative in chemical industry. In this Account, we have presented an emerging view of the solvent behavior of CO_2 based on recent experimental and theoretical studies. Although $scCO_2$ was originally considered as a nonpolar solvent comparable to alkanes because of its low dielectric constant and dipole moment, this view is slowly changing. The charge separation and electronic structure of CO_2 allows it to act as a Lewis acid or a Lewis base. Experimental and theoretical studies show that CO_2 can participate in conventional (red-shifting) and unconventional (blue-shifting) hydrogen bonds with various proton donor systems. This microscopic view of the solute−solvent interactions suggests that $scCO_2$ can be used as a solvent for several hitherto unknown molecular systems with considerable polarity. These "polar" attributes of CO_2 also have important consequences for new approaches to design functional solutes for use in CO_2 and in the design of suitable surfactants for the CO_2−H_2O interface. The CO_2-philic−hydrophilic balance required for formation of H_2O-in-CO_2 reverse microemulsions is a substantial challenge because some of the highly CO_2-philic functional groups can also have increased affinity for H_2O. In light of the present discussion, CO_2 still holds promise for being a more widely utilized, environmentally benign solvent in industrial applications because of its specific, nondipolar solvent attributes that are indeed polar in nature.

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