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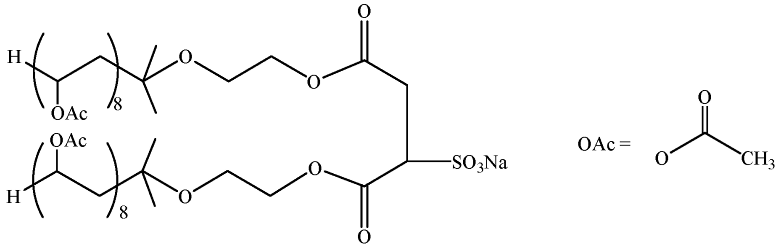

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Oxygenated Hydrocarbon Ionic Surfactants Exhibit CO_2 Solubility

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Abstract: Several oxygenated hydrocarbons, including acetylated sugars, poly(propylene glycol), and oligo(vinyl acetate), have been used to generate CO_2-soluble ionic surfactants. Surfactants with vinyl acetate tails yielded the most promising results, exhibiting levels of CO_2 solubility comparable to those associated with fluorinated ionic surfactants. For example, a sodium sulfate with single, oligomeric vinyl acetate (VAc) tails consisting of 10 VAc repeat units was 7 wt % soluble in CO_2 at 25 °C and 48 MPa. Upon introduction of water to these systems, only surfactants with the oligomeric vinyl acetate tails exhibited spectroscopic evidence of a polar environment that was capable of solubilizing the methyl orange into the CO_2-rich phase. For example, a single-phase solution of CO_2, 0.15 wt % sodium bis(vinyl acetate)8 sulfosuccinate, and water, at water loading (*W*) values ranging from 10 to 40 at 25 °C and 34.5 MPa, exhibited a methyl orange peak at 423 nm. This result indicated that the core of a reverse micelle provided a microenvironment with a polarity similar to that of methanol. Quantum chemical calculations indicate that the acetylated sugars may be too hydrophilic to readily form reverse micelles, whereas the VAc-based surfactants appear to have the correct balance of hydrophilic and hydrophobic forces necessary to form reverse micelles.

Introduction

Supercritical carbon dioxide (sc-CO_2) is a potential alternative to organic solvents in many chemical processes, because of its abundance, low cost, nontoxicity, nonflammability, and easily accessible critical conditions ($P_c = 7.38$ MPa, $T_c = 31.1$ °C). Unfortunately, sc-CO_2 is a feeble solvent. Although it can solubilize low molecular weight, volatile compounds at pressures below 10 MPa, polar and high molecular weight materials are usually poorly soluble at tractable pressures. One strategy for enhancing the capabilities of CO_2 as a green solvent has been the identification of additives, such as surfactants,[1,2] dispersants,[3,4] chelating agents,[5,6] thickeners,[7] and polymers,[4,8] that are designed to exhibit favorable thermodynamic interactions with CO_2. With regard to surfactants, nearly all conventional hydrocarbon-based ionic surfactants are essentially insoluble in sc-CO_2, however, because ionic headgroups are CO_2-phobic and hydrocarbon surfactant tails are not designed for favorable interactions with dense CO_2.[9] Ionic surfactants with CO_2 solubility of 1 wt % or more have been developed by incorporating highly CO_2-philic fluorinated tails or silicone-based tails, however. For example, perfluoropolyether (PFPE) sodium and ammonium carboxylates with average molecular weights of 2500, 5000, and 7500 were soluble in supercritical CO_2 at 40 °C and pressures below 17 MPa.[10] Fluoroalkyl-tailed sulfosuccinate surfactants, such as di-CF3, di-CF4, and di-CF6 stabilized microemulsions at CO_2 bottle pressure (5.7 MPa) at 15 °C, with a *W* value ([water]/[surfactant]) of 10.[11] Silicone-based ionic surfactants, such as a PDMS-based AOT analogue, can dissolve in CO_2 at 65 °C and pressures below 31 MPa.[12,13] Although these surfactants have been used successfully in supercritical fluid research, the environmental and biological persistence of these expensive fluorous and silicone-based

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surfactants has impeded their use in commercial applications. Less expensive, biodegradable, CO_2-soluble ionic surfactants capable of solubilizing water in the cores of reverse micelles could hasten the application of technologies that exploit water-in-CO_2 (w/c) microemulsions.

Recently, Eastoe and Johnston[14−16] described two branched hydrocarbon-based ionic surfactants, sodium bis(2,4,4-trimethyl-1-pentyl) sulfosuccinate and sodium bis(3,5,5-trimethyl-1-hexyl) sulfosuccinate, that exhibit CO_2 solubility. These twin-tailed sodium succinates are similar in structure to the CO_2-insoluble surfactant AOT, sodium bis(2-ethyl-1-hexyl) sulfosuccinate, but they contain trimethylpentyl or trimethylhexyl tails and are referred to as AOT-TMP and AOT-TMH, respectively. After extensive mixing, both AOT-TMP and AOT-TMH were shown to be slightly soluble in CO_2. This favored solvation of the branched tail surfactants by CO_2 may be attributable to the surface energy of the pendant methyl groups being much lower than that of the CH_2 groups of linear tails.[17] AOT-TMH reported has 0.1 wt % solubility in CO_2 at 40, 50, and 80 °C at 34.5, 31, and 29 MPa, respectively.[16]

There are several oxygenated hydrocarbon groups that exhibit more favorable thermodynamic interactions with CO_2 than branched alkanes, however. Acetylated sugars, such as per-acetylated glucose and galactose,[18] sorbitol,[19] maltose,[20] and cyclodextrins,[21] have been shown to dissolve in CO_2 at low pressures up to 10−50 wt %. Low molecular weight PPO (<2000) is quite CO_2-soluble at moderate temperature,[17] and higher MW PPO (>2000) is also soluble in CO_2 at elevated temperatures;[22] therefore, PPO has been used as a CO_2-philic segment in diblock and triblock nonionic surfactants along with hydrophilic blocks of poly(ethylene oxide) (PEO).[23,24] The solubility of the PPO oligomers has been attributed to the Lewis acid−Lewis base interaction between the ether oxygen in poly(propylene oxide) and the carbon in CO_2[25] and the lower surface tension caused by the pendent methyl group on each monomer unit favoring solvation by CO_2.[17] The lowering of the interfacial tension at the water−CO_2 interface, emulsion formation, and solubilities of block copolymers containing the PPO segment were reported.[17,26] Poly(vinyl acetate) is the most CO_2-soluble, high molecular weight, oxygenated hydrocarbon-based homopolymer that has yet been identified.[22,27] In the cases of poly(vinyl acetate) and the acetylated sugars, the high degree of CO_2 solubility has been attributed to a favorable two-point interaction between CO_2 and the accessible acetate side chain, a Lewis acid−Lewis base interaction between the C of the CO_2 and the O of the acetate carbonyl, and a weak, complimentary hydrogen bond between the O of the CO_2 and a proton on the methyl group of the acetate.[28,29] Recently, Stone and Johnston found that the interaction between CO_2 and CH_2 is about the same as CO_2 and CF_2.[30]

A level of 1 wt % surfactant soluble in CO_2, which would typically be needed for microemulsions, requires a moderately high, yet reasonable, pressure. Clearly, solubility is a key factor that governs whether a surfactant will lead to water-in-CO_2 microemulsions. An additional factor, steric force, which plays an important role in designing hydrocarbon surfactants for W/C microemulsions, has been described recently. Stubby tails enhance the formation of W/C microemulsions, as they raise surfactant solubility in CO_2 by weakening interactions between tails, weaken interactions between droplets, favor curvature of the interface bending toward water, and reduce the interfacial tension.[30−32] Ryoo and Johnston achieved about 1 wt % water, significant protein solubilities, and the presence of microemulsions as detected with dynamic light scattering formed by a methylated branched hydrocarbon nonionic surfactant. Furthermore, this study shows that the surfactant lowers the water−CO_2 interfacial tension significantly, which is an important requirement for forming microemulsions.[32]

The objective of this study was to design, synthesize, characterize, and evaluate the CO_2 solubility of ionic surfactants with oxygenated hydrocarbon tails composed of acetylated sugar, PPO, or oligo(vinyl acetate). Additionally, these surfactants were examined for their ability to form stable microemulsions with polar microenvironments capable of dissolving polar species in the bulk nonpolar CO_2 solvent. Figure 1 shows the structures of ionic surfactants investigated in this study. Ab initio quantum mechanical methods were used to complement the experimental work, adding a molecular-level view of the H_2O−surfactant and CO_2−surfactant interactions. Optimized geometries for either H_2O or CO_2 interacting with an isopropyl acetate molecule were computed, which is meant to model the repeat unit in the oligo(vinyl acetate) system. Similar calculations have been used by several groups to study the intermolecular interactions between CO_2 and model CO_2-soluble compounds.[18,25,28,33−36]

Experimental Section

Materials. All materials used to synthesize the ionic surfactants were purchased form Aldrich and used as received, unless otherwise noted. N_2 (99.995%) and CO_2 (99.99%, Coleman grade) were purchased from Penn Oxygen.

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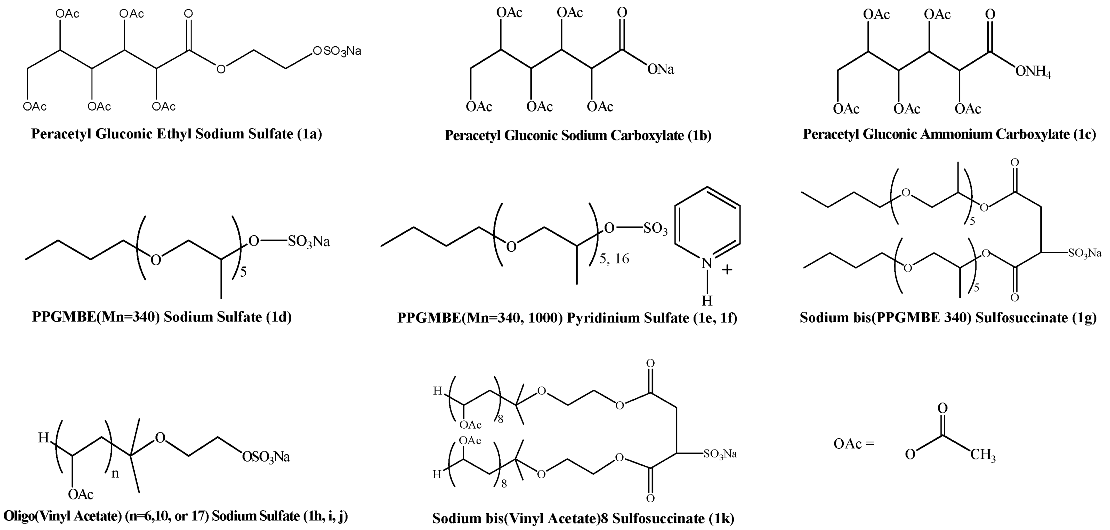

Figure 1. Ionic surfactants with oxygenated hydrocarbon tails.

Characterizations. The purities of the ionic surfactants were estimated by ^{1}H NMR spectra recorded on a Bruker 400 MHz NMR and IR spectra obtained on a Mattson Polaris FTIR. The molecular weights of the ionic surfactants were detected by mass spectra performed on a liquid chromatography/electrospray ionization/quadrupole time-of-flight mass spectrometer.

Surfactants Synthesis. Ionic Surfactants with Peracetyl Gluconic Tails (Figure 1a−c). Synthesis of Peracetyl Gluconic Carboxylic Acid. Acetic anhydride (30 mL) was cooled to about 15 °C, and 67% $HClO_4$ (4 g, 39.82 mmol) was then added to the cold acetic anhydride, followed by the addition of D-gluconate (5 g, 25.23 mmol). The temperature of the mixture was kept below 40 °C. After brief heating to obtain a homogeneous solution, the mixture was poured on ice and extracted twice with $CHCl_3$ (2×100 mL). The organic layers were pooled and washed with ice-cold water. Water (50 mL) and triethylamine (4 mL) were added to the $CHCl_3$, followed by overnight stirring to hydrolyze any anhydride. The organic layer was separated and washed with 1 N HCl and dried over anhydrous Na_2SO_4, and $CHCl_3$ was removed in vacuo to yield 80% 2,3,4,5,6-penta-*O*-acetyl-D-gluconic acid. ^{1}H NMR δ_H ($CDCl_3$): 5.618 (t, $J = 4.8$ Hz, 1H), 5.510 (dt $J = 6.4$ Hz, 1H), 5.285 (d, $J = 3.6$ Hz, 1H), 5.055 (m, 1H), 4.301 (dd, $J = 12.4$ Hz, 4 Hz, 1H), 4.113 (dd, $J = 12.4$ Hz, 5.6 Hz, 1H), 2.249 (s, 3H), 2.085 (s, 3H), 2.077 (s, 3H), 2.072 (s, 3H), 2.044 (s, 3H).

Synthesis of Peracetyl Gluconic Ethyl Sodium Sulfate (Figure 1a). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (4.8 g, 31.53 mmol) was added to a solution of peracetyl gluconate carboxylic acid (10 g, 24.63 mmol) and 2-bromoethanol (3.94 g, 31.53 mmol) in DMF(10 mL) and stirred at room temperature. After 12 h the mixture was poured into water (100 mL) and extracted with dichloromethane (3×50 mL). The organic layers were pooled, washed with water, and dried over anhydrous Na_2SO_4 prior to the removal of solvent. Column chromatographic purification of the crude product over silica gel using 50% ethyl acetate and hexanes as the eluent gave the pure product (9.4 g, yield 85%). The product was dissolved in anhydrous dichloromethane, pyridine sulfur trioxide (6.3 g, 39.58 mmol) was added, and the mixture was stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite and solvent removed to give the pyridinium salt. The pyridinium salt was dissolved in water (100 mL), and sodium bicarbonate (1.74 g, 20.71 mmol) was added. The resultant mixture was frozen and water was removed using a freeze-dryer to give a white color fluffy solid. HRMS (ESI): calculated for $C_{18}H_{25}Na_2O_{16}S$ ($[M + Na]^+$) 575.0659, found 575.0630.

Synthesis of Peracetyl Gluconic Sodium Carboxylate (Figure 1b). Peracetyl gluconic carboxylic acid (5 g, 12.32 mmol) was dissolved in water (50 mL), and sodium bicarbonate (1.04 g, 12.38 mmol) dissolved in water (10 mL) was added. The resultant solution was frozen and water was removed using a freeze-dryer to give white color fluffy solid. HRMS (ESI): calculated for $C_{16}H_{22}NaO_{12}$ ($[M + H]^+$) 429.1009, found 429.1016.

Synthesis of Peracetoxy Gluconic Ammonium Carboxylate (Figure 1c). Ammonium carbonate (2.0 g, 20.81 mmol) was added to a solution of peracetoxy gluconic carboxylic acid (5 g, 12.32 mmol) dissolved in water (50 mL), and the mixture was stirred. The resultant solution was frozen and water was removed using a freeze-dryer to give a yellow color fluffy solid. HRMS (ESI): calculated for $C_{16}H_{26}NO_{12}$ ($[M + H]^+$) 424.1455, found 424.1422.

Ionic Surfactants with PPG tails (Figure 1d−g). Synthesis of PPGMBE ($M_n = 340$) Sodium Sulfate (Figure 1d). Poly(propylene glycol) monobutyl ether ($M_n = 340$, 10 g, 29.4 mmol) was dissolved in dichloromethane (150 mL), pyridine sulfur trioxide (10 g, 62.83 mmol) was added, and the mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite and solvent removed to give the pyridinium salt. The pyridinium salt was dissolved in water (100 mL), and sodium bicarbonate was added until no further effervescence was observed. The resultant mixture was frozen and water was removed using a freeze-dryer to give yellow viscous liquid. Mass spectrum showed that the number-average molecular weight for PPGMBE ($M_n = 340$) sodium sulfate is 445.3.

Synthesis of PPGMBE ($M_n = 340, 1000$) Pyridinium Sulfate (Figure 1e,f). Poly(propylene glycol) monobutyl ether ($M_n = 340$, 10 g, 29.4 mmol) was dissolved in dichloromethane (150 mL), pyridine sulfur trioxide (10 g, 62.83 mmol) was added, and the mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite and solvent removed to give the PPGMBE ($M_n = 340$) pyridinium salt. PPGMBE ($M_n = 1000$) pyridinium sulfate was synthesized in the similar way. Mass spectra showed that the number-average molecular weight for PPGMBE ($M_n = 340$) pyridinium sulfate and PPGMBE ($M_n = 1000$) pyridinium sulfate is 515.2 and 1178.6, respectively.

Synthesis of Sodium Bis(PPGMBE 340) Sulfosuccinate (AOT Analogue) (Figure 1g). The esterification of alcohol and fumaryl chloride followed the procedure described by Nave et al.[14] Poly(propylene glycol) monobutyl ether ($M_n = 340$, 10.41 g, 30.62 mmol) and anhydrous THF (60 mL) were charged in a 250 mL three-neck round-bottom flask equipped with a stirring bar and condenser under a steady flow of nitrogen. After cooling to 0 °C, fumaryl chloride (2.81 g, 18.36 mmol) was added dropwise. The reaction mixture was stirred for the next 24 h at room temperature. After rotary evaporation of THF, the mixture was dissolved in 100 mL of diethyl ether and washed with 50 mL of 1 N HCl, 50 mL of saturated $NaHCO_3$, and 50 mL of saturated

Table 1. Experimental Data for PVAc−OH Oligomers from ^{1}H NMR at [AIBN]/[VAc] = 0.1%

	[VAc][a] (mol %)	DP_n (^{1}H NMR)	M_n (^{1}H NMR, g/mol)
PVAc6-OH	6.3	6	620
PVAc8-OH	8.2	8	792
PVAc10-OH	11.8	10	964
PVAc17-OH	18.6	17	1566

[a] Molar ratio of [VAc]/([VAc] + [2-isopropoxyethanol]).

NaCl solutions sequentially. The ether extract was dried over anhydrous Na_2SO_4 and filtered and then ether was removed by rotary evaporation. A pale yellow oil of diester product was obtained with 89% yield (10.37 g). The diester was subject to sulfonation with sodium hydrogen sulfite following the procedure provided by Baczko et al.[37] Sodium hydrogen sulfite (0.89 g, 8.55 mmol) in water (60 mL) was added dropwise to a solution of the diester (5 g, 6.58 mmol) in 2-propanol (80 mL) (both solutions were previously degassed with nitrogen for 20 min). The reaction mixture was then refluxed for the next 24 h. After rotary evaporation of the solvent, the residue was dissolved in chloroform and dried over Na_2SO_4 followed by removal of the solvent and drying of the resulting paste under a vacuum desiccator overnight. A yellow viscous liquid was obtained (4.2 g, yield 74%) The FTIR spectra showed the disappearance of the OH peak at 3500 cm^{-1} and appearance of carbonyl peak at 1750 cm^{-1}. Mass spectrum showed that the number-average molecular weight for sodium bis(PPGMBE 340) sulfosuccinate is 913.5.

Ionic Surfactants with Oligomeric Vinyl Acetate Tails (Figures 1h−k). Synthesis of Hydroxy-Functional Oligo(vinyl acetate). The 2,2′-azobisisobutyronitrile (AIBN) was recrystalized in methanol, and vinyl acetate was passed through an inhibitor remover column to remove the inhibitor prior to use. Oligomerization of vinyl acetate was carried out using AIBN as a free radical initiator with 2-isopropoxyethanol being both the solvent and chain-transfer agent. The preparation of hydroxy-functional oligo(vinyl acetate) followed the method of Zimmermann et al.[38] For a typical experiment, a solution of AIBN (0.04 g, 0.24 mmol) in 2-isopropoxyethanol (10 mL) (previously degassed for 15 min) was added to a solution of vinyl acetate (20 g, 232 mmol) in 2-isopropoxyethanol (190 mL) (previously degassed in a three-neck 500-mL round-bottom flask by bubbling through nitrogen for 30 min). The reaction mixture was refluxed at 90 °C under a N_2 blanket for 24 h. The solvent was removed by rotary evaporation followed by vacuum desiccation at 90 °C overnight. A viscous yellow liquid of hydroxyl-functional oligo(vinyl acetate) with 10 repeat units, designated PVAc10, was recovered (15.8 g, yield 79%). ^{1}H NMR δ_H ($CDCl_3$): 4.90 (10H, CH), 4.09 (2H, CH_2), 3.59 (2H, CH_2), 3.43 (1H, OH), 2.04 (30H, CH_3), 1.84 (20H, CH_2), 1.20 (6H, CH_3). ^{1}H NMR spectra showed $DP_n = 10$ and $M_n = 964$ g/mol. Table 1 lists the experimental data for the number of repeat units and number-average molecular weight of four PVAc−OH samples obtained from the NMR spectra by the polymerization of vinyl acetate in 2-isopropoxyethanol. The concentration of vinyl acetate monomer in 2-isopropoxyethanol was varied to control the molecular weight at constant concentration ratio of AIBN to VAc at 0.1%. Hydroxy-functional oligo(vinly acetate) with repeat unit of 6, 8, 10, and 17 as determined through NMR spectra were obtained and are represented as PVAc6−OH, PVAc8−OH, PVAc10−OH, and PVAc17−OH, respectively.

Synthesis of Oligo(vinyl acetate) Sodium Sulfate Surfactants (Figure 1h−j). The oligo(vinyl acetate) sodium sulfate surfactants were prepared according to Murphy and Taggart's procedure.[39] In a typical experiment, chlorosulfonic acid (0.45 mL, 6.76 mmol) was added dropwise to pyridine (10 mL) in a 250-mL round-bottom flask placed in an ice bath. The solution was stirred vigorously during the dropwise addition. A solution of hydroxy-functional oligo(vinyl acetate) PVAc10−OH (5 g, 5.19 mmol) in pyridine (50 mL) was slowly added to the above solution, and cooling and stirring were continued. The contents of the flask were refluxed for about 4 h until a clear yellow solution was formed. The reaction was then quenched and the product converted to the sodium salt by pouring the contents into an ice-cooled sodium hydroxide and sodium carbonate solution (0.27 g of NaOH and about 30−40 g of Na_2CO_3 in 100 mL of deionized water). The reaction mixture was stirred at room temperature for 3 h. The resulting oligo(vinyl acetate) surfactant solution was extracted using *n*-butanol (2 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. Evaporating the solvents pyridine and *n*-butanol by rotary evaporation followed by vacuum desiccation gave a dark yellow product, PVAc10−SO_3Na (4.86 g, yield 87.9%, M_n= 1066 g/mol).

Synthesis of Sodium Bis(vinyl acetate)8 Sulfosuccinate (Figure 1k). Twin-tailed oligo(vinyl acetate) AOT analogue was synthesized using the PVAc8−OH in a similar way as the PPGMBE (M_n = 340) twin-tailed AOT analogue that was described previously. A yellow, viscous liquid was recovered as product and confirmed by the disappearance of the FTIR peak at approximately 3500 cm^{-1} (−OH) and the appearance of the carbonyl peak at 1741 cm^{-1}.

Phase Behavior Measurement. A known amount of surfactant (e.g., 0.0700 ± 0.0001 g) was loaded into the sample volume of a high pressure, windowed, stirred, variable-volume view cell (DB Robinson & Assoc., 3.18 cm i.d., ~120 cm^3 working volume). In this cell, the sample volume is separated from the overburden fluid by a steel cylinder (floating piston) that retains an O-ring around its perimeter. The O-ring permits the cylinder to move while a seal is retained between the sample volume and the overburden fluid. After purging with carbon dioxide at 0.2 MPa, the sample volume was minimized by displacing the floating piston to the highest possible position within the cell that did not result in the displacement of surfactant out of the sample volume. High-pressure liquid carbon dioxide (24 °C, 13.8 MPa) was then introduced to the sample volume as the silicone oil overburden fluid (which was maintained at the same pressure as the CO_2) was withdrawn at the equivalent flow rate using a dual-proportioning positive displacement pump (DB Robinson). This technique facilitated the isothermal, isobaric addition of a known volume of CO_2 (e.g., 12.50 ± 0.01 mL) into the sample volume. The mass of CO_2 introduced was determined from the displaced volume, temperature, and pressure using an accurate equation of state for carbon dioxide.[40] On the basis of the uncertainties associated with the measurement of temperature, pressure, and volume, and the precision of the equation of state, compositions are estimated to be accurate to within 1% of the specified value (e.g., 0.5 ± 0.005 wt %).

The surfactant−CO_2 mixture was compressed to high pressure (e.g., 60 MPa) and mixed thoroughly using a magnetic stirrer (DB Robinson, max. 2500 rpm). If the surfactant did not completely dissolve at these conditions, additional CO_2 was added to the system until a single transparent phase could be attained. Cloud points were determined by standard nonsampling techniques. The high-pressure, single-phase solution of known composition was subjected to a slow, isothermal expansion until the cloud point was attained. Cloud points were reproduced three times to within approximately ±0.1 MPa for monodisperse surfactants and ±0.5 MPa for polydisperse surfactants. Temperatures were measured with a type K thermocouple to an accuracy of ±0.1 °C.

Experiments with water were conducted by adding the specified amount of surfactant and double distilled and deionized water to the sample volume, followed by the introduction of CO_2. *W* is the molar ratio of water to surfactant in the mixture.

Dye Solubilization and Spectroscopic Measurements. A 32-mL stainless steel high-pressure vessel equipped with pressure gauge,

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resistance temperature detector (RTD), and parallel quartz windows for UV−vis characterization, which has been described previously,[41] was used to perform dye solubilization experiments. A magnetic stir bar was used to facilitate surfactant/CO_2 mixing. For a typical experiment, 100 μL of freshly prepared 0.015 M methyl orange (MO) in methanol solution was added into the UV cell, and a gentle stream of N_2 was passed through the cell for 10 min to fully evaporate the methanol while only the MO inside of the UV cell was maintained. Then 0.15 wt % of surfactant was charged into the cell and a specific amount of double distilled and deionized water was injected into the cell using a syringe to reach the desired W value. After sealing the vessel, an ISCO syringe pump was used to add a specific quantity of CO_2 to the vessel. Once the vessel was filled with CO_2 to the desired pressure, the system was mixed for at least an hour to reach a single phase before performing spectroscopic analysis. The vessel was placed in a Cary 300E UV−vis spectrophotometer and absorption spectra were recorded to determine the presence of methyl orange solubilized in the surfactant/water/CO_2 mixture. Pressure within the vessel was monitored to approximately ±0.7 MPa, and temperature was maintained to within ±0.1 °C.

The ability to form reverse micelles by these CO_2-soluble surfactants was investigated using the solvatochromic probe methyl orange at system concentration of ca. 4.7×10^{-5} M. Methyl orange is a polar probe that is insoluble in both carbon dioxide and water-saturated carbon dioxide. Furthermore, the location of its absorption maximum is dependent upon the polar environment in which it is dissolved. For instance, it has an absorption maximum at 416 in dry PFPE-NH_4/CO_2 reverse micelles, 421 in methanol, 464 in water, and 502 nm in CO_2-saturated water.[42,43] Hence, the solubility of methyl orange in an otherwise ineffective solvent, such as CO_2, indicates the presence of reverse micelles and it also functions as a probe of polarity of the water environment within CO_2 reverse micelles. Consequently, methyl orange has been used successfully to identify the presence of reverse micelles as well as their ability to uptake water in CO_2 reverse micelles.[42−49] It was indicated that the absorption maximum in water-in-CO_2 microemulsions formed by PFPE ammonium carboxylate surfactant approaches that of pure water ($\lambda_{max} = 460$ nm).[50] While a surfactant may show some solubility in CO_2 in the presence of dissolved water, this alone does not guarantee that a polar microenvironment is present. Verification of a polar microenvironment is necessary to confirm that the surfactant does indeed self-assemble in solution to form reverse micelles.

Molecular Modeling. High-level ab initio methods cannot be directly applied to modeling fluid−surfactant interactions because of the large number of atoms in the system. Representative segments or moieties of the surfactant tails were chosen to perform calculations for H_2O and CO_2 interacting with these segments. We focus only on the acetate-functionalized surfactants, choosing isopropyl acetate as representative of the functional groups for molecules **1a**−**c** and **1h**−**k**.

The acetate/H_2O complex involves hydrogen bonding between the H_2O and the acetate oxygens. Therefore, Møller−Plesset second-order perturbation theory (MP2) is expected to give an accurate representation of the potential energy surface.[25,51−54]

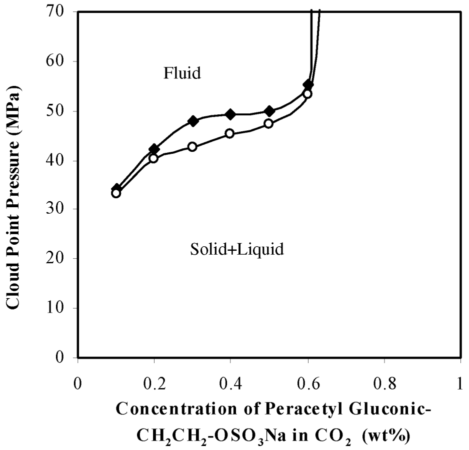

Figure 2. Phase behavior of peracetyl gluconic−CH_2CH_2−OSO_3Na/CO_2 mixtures. Insoluble at $W = 0$; 25 °C, $W = 10$ (◆); 40 °C, $W = 10$ (○).

Geometry optimizations were carried out at the MP2/6-31+g(d) level of theory and basis set. The 6-31+g(d) basis set was chosen for computational efficiency. Single-point energy calculations were performed by using the Dunning aug-cc-pVDZ basis set,[55] and using geometries obtained from optimizations. Counterpoise (CP) corrections[56] were applied to all the calculations to account for basis set superposition error, which has considerable impact on the accuracy of results for weakly binding systems.[33] The average of raw and CP corrected energies was used as an approximation to energies at the complete basis set limit, which was shown to be accurate for CO_2/acetate systems[25] and also in agreement with the findings of Feller and Jordan.[57] Hence, in this paper, we only report the averages of MP2/aug-cc-pVDZ CP corrected and uncorrected interaction energies. The Gaussian 03[58] software package, revision C.01, was used for all the calculations.

Results and Discussion

Phase Behavior Results and Discussion. Peracetyl Gluconic-Based Surfactants (Figure 1a−c). The neat peracetyl gluconic-based surfactants with an ethyl spacer and a sodium sulfate, sodium carboxylate, or ammonium carboxylate headgroup (Figure 1a−c) are solids. Peracetyl gluconic ethyl sodium sulfate (PGESS) does not dissolve in CO_2 at 25 or 40 °C in the absence of water ($W = 0$), but its solubility increases as water is added, as shown in Figure 2. The surfactant is up to 0.6 wt % soluble in CO_2 in the presence of water at a W value of 10. At W values of 40 and 50, however, a water phase appeared at the bottom of the cell. Attempts to dissolve 0.7 wt % or more yielded an excess surfactant-rich phase at the bottom of the cell for all values of W.

Figure 3 shows that peracetyl gluconic sodium carboxylate (PGSC) appears to be more CO_2 soluble than PGESS, because PGSC can dissolve at 40 °C in the absence of water. The solubility of PGSC decreases slightly with the addition of water.

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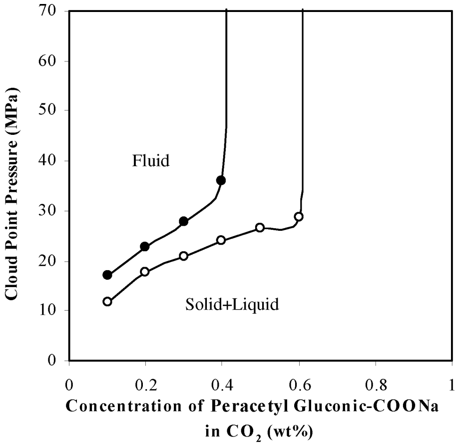

Figure 3. Phase behavior of peracetyl gluconic−COONa/CO_2 mixtures at 40 °C. $W = 0$ (○); $W = 10$ (●).

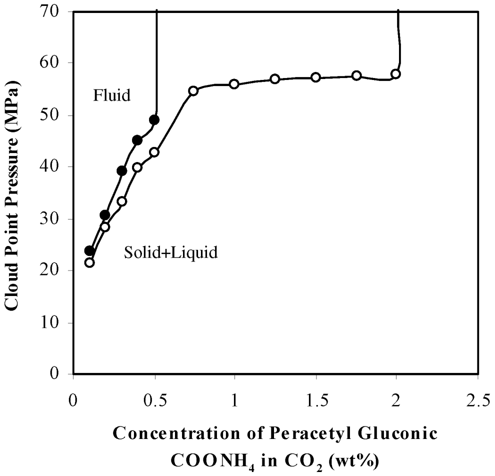

Figure 4. Phase behavior of peracetyl gluconic−$COONH_4$/CO_2 mixtures at 40 °C. $W = 0$ (○); $W = 10$ (●).

PGSC has a limiting solubility of approximately 0.4 wt % in CO_2 at $W = 10$. Single phase solutions could not be realized at W values of 40, even at surfactant concentrations as low as 0.1 wt %.

Figure 4 illustrates that peracetyl gluconic ammonium carboxylate (PGAC) can dissolve in CO_2 up to 2 wt % at 40 °C without water. Although this limiting solubility value is significantly greater than those for either PGESS or PGSC, the pressure required to dissolve PGAC at dilute concentrations (up to 0.5 wt %) was greater than that required to dissolve PGSC. The solubility of PGAC decreases with the introduction of water, as does its limiting solubility in CO_2, which is about 0.5 wt % at W value of 10. Single-phase solutions could not be realized at W values of 40, even at surfactant concentrations as low as 0.1 wt %.

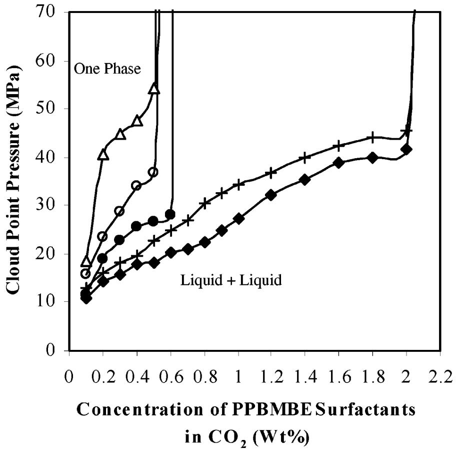

Figure 5. Phase behavior of PPGMBE surfactants/CO_2 mixtures at 40 °C. PPGMBE 340 sodium sulfate, $W = 0$ (△); PPGMBE 1000 pyridium sulfate, $W = 0$ (○); PPGMBE 1000 pyridium sulfate, $W = 10$ (●); sodium bis(PPBMBE 340) sulfosuccinate, $W = 0$ (◆); sodium bis(PPBMBE 340) sulfosuccinate, $W = 10$ (+).

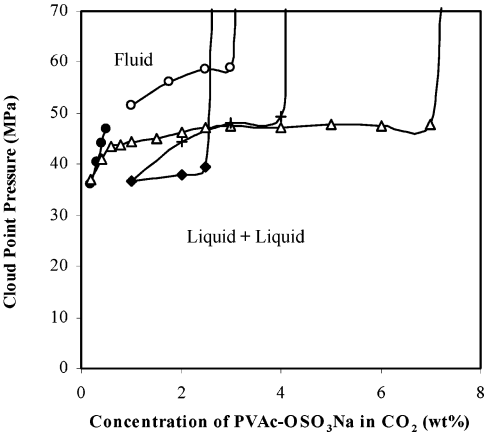

Figure 6. Phase behavior of PVAc−OSO_3Na/CO_2 mixtures. PVAc6−OSO_3Na, 25 °C, $W = 0$ (+); PVAc10−OSO_3Na, 25 °C, $W = 0$ (△); PVAc17−OSO_3Na, 25 °C, $W = 0$ (◆); PVAc10−OSO_3Na, 25 °C, $W = 10$ (●); PVAc10−OSO_3Na, 40 °C, $W = 0$ (○).

Poly(propylene glycol) Monobutyl Ether-Based Surfactants (Figure 1d−g). The PPGMBE 340 pyridinium sulfate was insoluble in CO_2. Figure 5 illustrates that the PPGMBE 340 sodium sulfate is CO_2-soluble, however, indicating that the sodium counterion is less CO_2-phobic than the pyridinium counterion. The PPGMBE 1000 pyridinium sulfate can dissolve in CO_2, indicating that the longer PPG segment of the tail made the surfactant with the pyridinium sulfate more CO_2 soluble. The addition of water lowers the cloud point pressure, as shown by the PPGMBE 1000 pyridinium sulfate dissolving in CO_2 at 40 °C and concentrations of 0.1−0.6 wt % at $W = 10$. In each case, the limiting solubility of this surfactant in CO_2 is approximately 0.5 wt %. Single-phase solutions could not be realized at W values of 40, even at surfactant concentrations as low as 0.1 wt %.

The phase behavior of mixtures of CO_2 and a twin-tailed sodium bis(PPBMBE 340) sulfosuccinate (Figure 1g) was also determined. This PPG twin-tailed AOT analogue surfactant is 2 wt % soluble in CO_2, and its solubility in CO_2 decreases with the addition of water at W value of 10, as shown in Figure 5. Single-phase solutions could not be realized at W values of 40, even at surfactant concentrations as low as 0.1 wt %.

Oligo(vinyl acetate)-Based Surfactants (Figure 1h−k). Single-Tailed Oligo(vinyl acetate) Sodium Sulfate Surfactants (Figure 1h−j). Viscous liquid oligo(vinyl acetate) sodium sulfate surfactants (M_n = 722, 1066, 1668 g/mol) exhibit remarkably high solubility in CO_2, as shown in Figure 6. These levels of CO_2 solubility for an ionic surfactant are comparable to those reported for fluorous surfactants,[10] greater than the other oxygenated hydrocarbon surfactants developed during this work, and greater than those reported for branched hydrocarbon AOT analogues.[16] The PVAc−OSO_3Na surfactants consisting of 6, 10, or 17 repeat units exhibit CO_2 solubility of 4, 7, and 2.5 wt

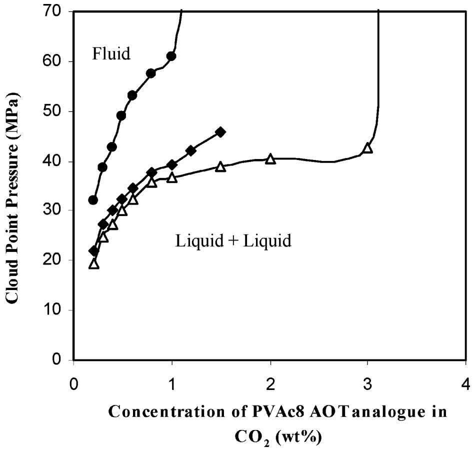

Figure 7. Phase behavior of sodium bis(vinyl acetate)8 sulfosuccinate/CO_2 mixtures at 25 °C. $W = 0$ (△); $W = 10$ (◆); $W = 50$ (●).

%, respectively, at room temperature and pressure less than 50 MPa. The occurrence of an optimal tail length, 10 repeat units in this case, has been previously observed in the design of surfactants with PFPE tails and can be attributed to two competing trends. As the number of repeat units in vinyl acetate oligomer decreases, the oligomer itself becomes more CO_2 soluble; however, as the length of the oligomeric tail decreases, the surfactant becomes more hydrophilic (and CO_2-phobic) as the influence of the ionic group becomes more pronounced.[59]

The solubility of oligo(vinyl acetate) surfactant decreases with increasing temperature, i.e., the pressure required to achieve miscibility with CO_2 is higher at 40 °C than it is at 25 °C, as represented in Figure 6. The solubility of the oligo(vinyl acetate) surfactant in CO_2 also decreases with the addition of water at a W value of 10. The surfactant solubility drops to 0.5 wt % under these conditions. Single-phase solutions could not be realized at W values of 40, even at surfactant concentrations as low as 0.1 wt %.

Twin-Tailed Sodium Bis(vinyl acetate)8 Sulfosuccinate (1k). The sodium bis(vinyl acetate)8 sulfosuccinate AOT analogue consisting of twin tails of eight repeat units on each tail ($M_n = 1768$ g/mol) was a viscous liquid that exhibited CO_2 solubility up to 3 wt % at 25 °C and pressure less than 40 MPa, as shown in Figure 7. The solubility decreases with the addition of water at $W = 10$. This surfactant was the only one (of those illustrated in Figure 1) capable of solubilizing water to W values as high as 50, at surfactant concentrations up to 1 wt %.

Spectroscopic Results and Discussion. The peracetyl gluconic surfactants were examined at 0.3 wt % in CO_2 at 40 °C and with water loading of $W = 10$. In each case, the CO_2-surfactant solutions were compressed to pressures above the reported cloud point pressure. Specifically, the sodium carboxylate, ammonium carboxylate, and ethyl sodium sulfate forms of the peracetyl gluconic were pressurized to 38, 44.8, and 48.3 MPa, respectively. There was no apparent methyl orange absorption, however, indicating that there was no tendency of the surfactants to form reverse micelles or polar microenvironments. Visual observation showed that, while water was dissolved into the CO_2, dry methyl orange was being left on the surface of the vessel, thus indicating that none of the water in the CO_2-rich phase existed in the form of a bulk water pool within the core of reverse micelles.

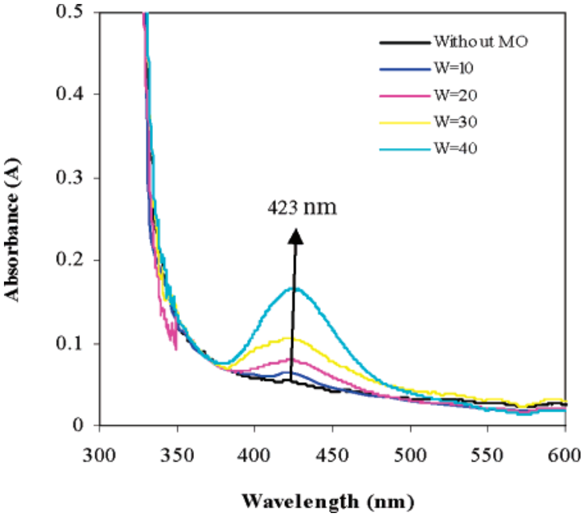

Figure 8. UV−vis absorption spectra of methyl orange in 0.15 wt % twin-tailed sodium bis(vinyl acetate)8 sulfosuccinate based water-in-CO_2 reverse microemulsions with different loading of water at 34.5 MPa and 25 °C.

It was difficult to attain a single-phase solution with the PPG-based surfactants, possibly due to the less intense mixing in the UV−vis cell and/or the instability these surfactants exhibited during the weeks between their synthesis and their evaluation for water uptake. Therefore, no evidence of reverse micelle formation was obtained for these surfactants.

The single tailed PVAc10−OSO_3Na was loaded at 0.15 wt % with water loading of $W = 10$ ($W^{corr} = 0$, 0.025 wt %) and methyl orange at 4.7×10^{-5} M. The system was pressurized to 38 MPa at 25 °C and stirred for 1 h. After this mixing period, a methyl orange peak was observed at 422 nm, implying the formation of water-in-CO_2 (w/c) reverse microemulsions. The twin-tailed sodium bis(vinyl acetate)8 sulfosuccinate AOT analogue was loaded at 0.15 wt % with a water loading of $W = 10$, 20, 30, and 40, respectively, (0.015 wt %, 0.03 wt %, 0.045 wt %, and 0.06 wt %, respectively) at $W^{corr} = 0$, and methyl orange at 4.7×10^{-5} M. After pressurizing to 34.5 MPa at 25 °C, the system was allowed to mix for over 1 h to reach a single phase microemulsion. Figure 8 shows the UV−vis spectra for the twin-tailed sodium bis(vinyl acetate)8 sulfosuccinate w/c reverse microemulsion system. As shown in Figure 8, the UV absorption peaks assigned at about 423 nm indicate the formation of the water-in-CO_2 reverse microemulsions. The intensity of the methyl orange peak increases with the water loading ranging from $W = 10$ to 40, which indicates that the concentration of methyl orange within the microemulsions increases as the amount of water loading increases. However, the absorption maximum wavelength, λ_{max}, does not shift to higher wavelengths, which implies that the polarity of the microenvironment within the reverse micelles does not increase with the increasing amounts of water loaded to the system. Methyl orange dissolved in bulk water results in an absorption maximum wavelength at 464 nm. The absorption bands of ∼423 nm in these studies indicate that the microenvironment within the reverse micelles of the ionic surfactants with PVAc tails is similar to that of neat methanol (methyl orange absorption at ∼421 nm) and slightly more polar than that of the cores of dry PFPE−COO−NH_4 reverse micelles (∼416 nm).[42,43] Whereas the twin-tailed vinyl acetate based surfactants lead to high water loading values up to $W = 50$, the methyl orange solubilities

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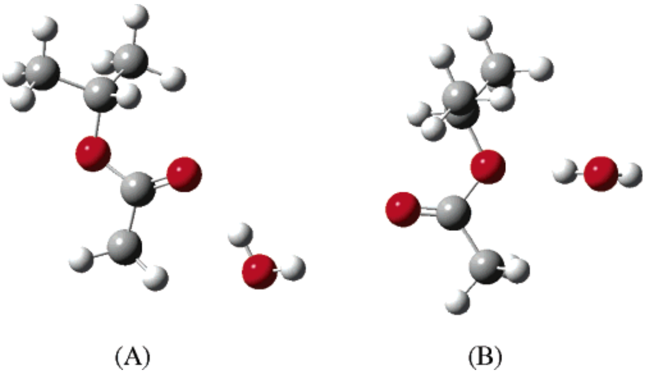

(A) (B)

Figure 9. Two different binding modes for the isopropyl acetate/H_2O system. (White = H, gray = C, red = O).

Table 2. Interaction Energies[a] for Several Different Dimers Related to the CO_2/H_2O Surfactant Systems

	IPA/H_2O					CO_2/CO_2	
	A	B	IPA/ CO_2[b]	H_2O/ H_2O[52]		T-shape	slipped parallel
interaction energy (kJ/mol)	−27.0	−21.3	−15.9	−19.6	−20.7[c]	−5.1	−5.8

[a] The energies are computed at the MP2/aug-cc-pVDZ level of theory. [b] There are actually three binding modes for the IPA/CO_2 dimer. We chose the mode that has the strongest interaction energy for comparison.[25] [c] The value is calculated at the MP2 level of theory and extrapolated to the complete basis set limit.[52]

and polarities are rather limited. This can be attributed to the relatively low corresponding weight percent of water caused by the low surfactant loading concentration, the high molecular weight, and the $W^{corr} = 0$ under these conditions, which means the amount of water added to the system would be insufficient to saturate the CO_2.

Modeling Results and Discussion. We have optimized the geometries and calculated the binding energies for a single water molecule interacting with an isopropyl acetate (IPA) molecule. Two different binding modes were found for the IPA/H_2O system. As shown in Figure 9, for mode A, the water molecule mainly interacts with the carbonyl oxygen. For mode B, H_2O binds mainly with the ether oxygen. The interaction energies for the two modes are listed in Table 2.

The interactions between IPA and water molecules as shown in Table 2 are much stronger than the strongest binding energy between IPA and CO_2.[25] Our calculations therefore predict that the tails of the acetate-functionalized surfactants (**1a**−**c**,**h**−**k**) are hydrophilic. Furthermore, we predict that the peracetyl surfactants have a higher affinity for water than the PVAc-based surfactants, because the tail backbone, which is hydrophobic, is completely shielded from the solvent by the acetyl groups. Experiments were performed to measure the water solubility of peracetyl gluconic sodium carboxylate (**1b**), peracetyl gluconic ammonium carboxylate (**1c**), and oligo(vinyl acetate)10 sodium sulfate (**1i**). A 20-μL portion of water was initially added to 0.08 g of surfactant (80 wt %) and then water was gradually added to the mixture followed by stirring the mixture using a Vortex-Genie 2 mixer until the surfactant was completely dissolved. The measured solubilities are reported in Table 3 and clearly show that both peracetyl surfactants are significantly more water soluble than the vinyl acetate-based surfactant. The headgroups on the peracetyl- and vinyl acetate-based surfactants are not identical. However, the sodium sulfate headgroup of **1i** should make that surfactant more water soluble than the headgroups of **1b** and **1c**. Therefore, we expect that the differences in water solubility due to the composition of the tail groups are larger than those of the headgroups, as indicated by the data in Table 3. The experimental solubility values are in good qualitative agreement with the trends predicted from our ab initio calculations.

Table 3. Water Solubility Values of Three Acetate Functionalized Surfactants

surfactant	water solubility (wt %)
peracetyl gluconic sodium carboxylic (**1b**)	64
peracetyl gluconic ammonium carboxylic (**1c**)	73
oligo(vinyl acetate)10 sodium sulfate (**1i**)	40

The Effects of the Addition of Water in Surfactants/CO_2 Systems. Our calculations indicate that the addition of water to CO_2 mixtures containing acetate-based surfactants will result in an increase in the cloud point pressures. Water molecules will compete with CO_2 molecules for binding to the acetate groups. The acetate tail groups will preferentially bind with water molecules because of the more favorable binding energies (see Table 2), thus lowering the CO_2 solubilities of the surfactants.

Experiments have shown that the addition of water does indeed increase the cloud point pressures of two of the peracetyl gluconic-based surfactants (**1b**,**c**) and also of the PVAc single/twin tailed surfactants (**1h**−**k**). These observations are consistent with our theoretical analysis. However, PGESS (**1a**) exhibits the opposite behavior, which could not dissolve in CO_2 in the absence of water, and its solubility increases as water is added. This may be due to cosolvent effects with water. PGESS is insoluble in CO_2 because of its extremely polar headgroup. Adding water to the PGESS/CO_2 system acts to shield the sulfate headgroup from CO_2 and therefore increases the solubility. Therefore, water plays competing roles in the PGESS/CO_2 system. On one hand, it increases solubility by shielding the headgroup from the nonpolar CO_2 environment. On the other hand, water competes with CO_2 in binding to the CO_2-philic acetate tail.

The Formation of the Reverse Micelles. The experiments have shown that only the PVAc-based surfactants can form reverse micelles. None of the peracetyl gluconic-based surfactants exhibit micelle formation, although their tail groups have similar structures to those of PVAc-based surfactants. The formation of micelles requires a tail that is sufficiently hydrophobic to drive water out of the bulk homogeneous phase into confined micelles. Our calculations indicate that the peracetyl tails are very hydrophilic. We therefore speculate that peracetyl tails do not have a large enough hydrophobic driving force to form micelles. In contrast, the methylene groups in the PVAc tails are relatively hydrophobic, which provides enough of an energetic driving force to stabilize the micelles. The difference in water solubilities of peracetyl gluconic-based surfactants and PVAc-based surfactants (Table 3) indicates that peracetyl tails are indeed more hydrophilic than PVAc tails. The difference in water solubilities provides a plausible explanation for the observation that PVAc-based surfactants form micelles while the surfactants with peracetyl gluconic tails do not.

Conclusions

Ionic surfactants with CO_2-philic tails composed of sugar acetate, poly(propylene glycol), or oligo(vinyl acetate) were found to be CO_2 soluble. Oligo(vinyl acetate)-functionalized surfactants were particularly promising, with the single-tailed surfactants exhibiting CO_2 solubility levels of 2−7 wt %, while the twin-tailed surfactant was 3 wt % soluble in CO_2. As water was introduced to these systems, the solubility of all of the (vinyl acetate)-functionalized ionic surfactants decreased to levels of 0.5−1.5%. Although the single-tailed surfactants could only attain a single phase at W values less than 10, water loading values of 50 were attained with the twin-tailed sodium bis(vinyl acetate)8 sulfosuccinate AOT analogue at surfactant concentrations as high as 1 wt %. Further, spectroscopic analysis indicated that only the single-tailed oligo(vinyl acetate) ionic surfactants and the AOT analogue with twin oligo(vinyl acetate) tails established a polar microenvironment within CO_2 comparable in polarity to methanol. Ab initio modeling was performed to address the question of why the oligo(vinyl acetate) tails form polar microenvironments while the peracetyl gluconic tails, which are similar, do not. The calculations indicate that the acetate group is very hydrophilic, preferring to bind with H_2O over CO_2. We therefore speculate that the peracetyl tails do not have a sufficiently high hydrophobic driving force to form reverse micelles. In contrast, the oligo(vinyl acetate) tails have both hydrophilic and hydrophobic (methylene backbone) sections, which provide the correct balance of forces necessary to drive water out of the bulk phase into reverse micelles.

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Supporting Information Available: Complete ref 58. This material is available free of charge via the Internet at http://pubs.acs.org.

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