J. Phys. Chem. A **2003,** *107,* 11239−11244

An FT-IR Study of Crown Ether−Water Complexation in Supercritical CO_2

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Received: June 24, 2003; In Final Form: September 25, 2003

In the presence of 18-crown-6, D_2O forms a 1:1 complex with the macrocyclic molecule in supercritical fluid CO_2 with two different configurations. The D_2O molecule can be bonded to two oxygen atoms of the crown cavity in a bridged configuration that is characterized by a broad peak at 2590 cm^{-1}. The D_2O molecule can also form one hydrogen bond with an oxygen atom of the crown cavity that can be characterized by two peaks at 2679 and 2733 cm^{-1}, with the former assigned to the hydrogen-bonded O−D stretching and the latter the unbonded O−D stretching. The equilibrium constants of the two configurations in supercritical CO_2 have been calculated. The enthalpy of formation is -12 ± 2 kJ mol^{-1} for the single-hydrogen-bond complex and -38 ± 3 kJ mol^{-1} for the bridged configuration complex. At high 18-crown-6 to D_2O ratios, the formation of another complex in supercritical CO_2 that involves one D_2O molecule hydrogen bonded to two 18-crown-6 molecules becomes possible.

Introduction

Supercritical fluids have unique properties that make them highly attractive for extraction of metal ions from liquid and solid materials.[1−3] Carbon dioxide is most widely used for supercritical fluid applications because of a number of advantages including (i) low toxicity, (ii) environmentally benignity, (iii) low cost, (iv) moderate critical constants ($T_c = 31$ °C and $P_c = 73.7$ bar), and (v) tunable solvation strength that varies with density. Selective extraction of metal species using a nonpolar solvent such as CO_2 requires special chelating agents that should possess ion recognition ability and be soluble in supercritical fluid carbon dioxide (SF-CO_2).[1−3] Crown ethers have been extensively used for extraction of alkali-metal and alkaline-earth-metal cations from aqueous solutions into organic solvents.[4−9] The relatively high solubility of crown ethers in liquid and supercritical CO_2 and their selectivity for the alkali-metal and the alkaline-earth-metal ions make them attractive for environmental applications such as CO_2-based nuclear waste management technology that would result in minimum liquid waste generation.

For the extraction of metal ions from aqueous solutions using ligands dissolved in SF-CO_2, the fluid phase will be saturated with water. Thus, water interaction with the ligand in the fluid phase plays an integral role in the extraction process.[2,9] It has been reported that the extraction efficiency of alkali-metal ions in conventional solvent processes depends on the solubility of water in the organic phase using macrocyclic polyethers as a complexing agent.[9] With crown ethers, both computational simulation[10] and spectroscopic studies[11,12] show that, in organic solvents, the water can bond to a macrocyclic host molecule by two different types of hydrogen bonding. The first type is composed of a single hydrogen bond between one hydrogen atom of a water molecule and one oxygen atom of the crown ether cavity. In this case, the water molecule is mostly located outside the cavity. The second type occurs inside the cavity and is composed of a water molecule bridging between two different oxygen atoms of the crown cavity.

FT-IR is a sensitive and qualitative technique that has been used during the past few years to study hydrogen bonding in different solvents.[12−16] For example, Fulton et al.[13] used this technique to explore hydrogen bonding of methanol dissolved in supercritical carbon dioxide and found that a weak interaction between carbon dioxide and methanol significantly reduced the amount of methanol−methanol hydrogen bonding. Johnston et al. used it to understand the solvent effect on hydrogen bonding in supercritical fluids.[14] They were able to determine, with a good accuracy, the equilibrium constants and other thermodynamics data for the hydrogen bond between methanol and triethylamine. The FT-IR technique has also been used by Moyer et al.[12] to determine how water is bonded to crown ethers in carbon tetrachloride. These authors assigned vibrational bands to free water and to two different kinds of hydrogen bonds mentioned above. In this paper we examine the interactions of water and 18-crown-6 in liquid and supercritical CO_2 for the purpose of establishing a basis for using this green solvent in extraction processes utilizing crown ethers as extractants.

Experimental Section

A specially designed high-pressure IR cell capable of operation to 500 bar was used for this study. The 9.2 mL internal volume cell is built in stainless steel block. The infrared beam is focused along two conical holes and passes through two small diamond windows providing a path length of 100 μm. The cell has one observation window (sapphire) sealed with a gold-plated metal V-ring seal, which allows visual determination of the number of phases present inside the cell. For quantitative analysis it is essential to avoid formation of a second aqueous phase on the beam path windows, which would interfere with data collection. A Teflon-coated magnetic stirring bar was introduced into the cell, allowing stirring of the solution while the cell was placed inside an FT-IR spectrometer.

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10.1021/jp035798y CCC: \$25.00

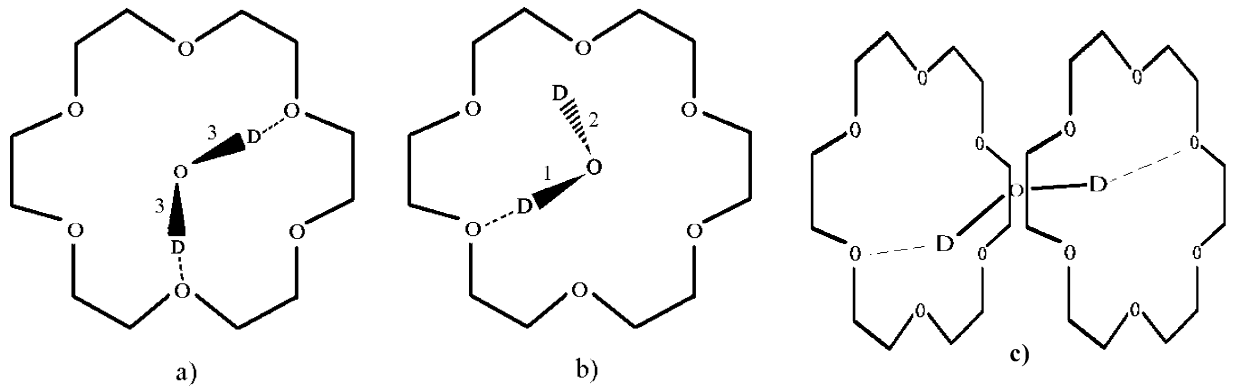

Figure 1. Scheme of the three possible bondings between D_2O and 18-crown-6: (a) bridge bonding; (b) single bonding; (c) 1:2 complex in a sandwich configuration.

A syringe pump (ISC0, model 100DX) was used to supply liquid CO_2 to the cell that was preloaded with the starting chemicals. The pressure was measured using an electronic transducer (Precise Sensor Inc., model D451-10) with a ±1 bar accuracy. The cell was placed on a lightweight ceramic stand, thermally isolated with an insulation coat, and heated using four electric cartridge heaters. The temperature was controlled with a controller (Watlow) having a ±1 °C accuracy. A Bruker IFS 66v FT-IR spectrometer with a mercury−cadmium−telluride (MCT) detector (Kolmar Technologies) was used to acquire all IR spectra. To obtain a good signal-to-noise ratio, the acquisition time was set at 5 min (corresponding to approximately 2350 scans), the scanner velocity was 80 kHz set for 4 cm^{-1} resolution. A background spectrum of the empty cell (with diamond windows) was subtracted from each sample spectrum. Deuterated water (D_2O) was used rather than H_2O to avoid overlapping of water and intense CO_2 absorption bands between 3500 and 3800 cm^{-1}. The existence of weak 18-crown-6 bands between 2760 and 2680 cm^{-1} (C−H stretch) which overlap with the D_2O signal required a spectrum of the pure crown ether in CO_2, at the same temperature and pressure, to be subtracted from the sample spectrum for background correction.

D_2O (100% D, 99.96% pure), 18-crown-6 (99.5% pure), dicyclohexano-18-crown-6 (98% pure), methanol-*d* (99.5+ atom % D), and carbon tetrachloride (99.9% pure) were purchased from Aldrich Chemical Co. and used without further purification. Carbon dioxide was obtained as supercritical fluid chromatography (SFC) grade (purity >99.99%) from Scott Specialty Gases Inc. The pure CO_2 density varies in this study between 0.66 and 1.04 g mL^{-1} by tuning the temperature between 25 and 70 °C and the pressure between 200 and 400 bar. The pure CO_2 density was determined using a reported table from the NIST (National Institute of Standards and Technology) Chemistry WebBook.

To avoid water contamination from the atmosphere, the cell was purged with nitrogen and the chemicals were handled and introduced using a glovebox purged with nitrogen. The solutions were stirred for 20−30 min to reach equilibrium after each density or concentration change. Longer equilibrium times were briefly explored, but no significant change in the IR spectra was observed. Curve fitting and other spectrum analysis and corrections have been performed with standard spectral software (OPUS, Bruker Optiks).

Results and Discussion

To study the nature of crown−water hydrogen bonding in liquid and SF-CO_2, we examined FTIR spectra of a series of mixtures with 18-crown-6 concentrations varied from 0 to 0.25 mol L^{-1} and the total D_2O concentration fixed at 49 mmol L^{-1}. The D_2O concentration was below the known solubility of water in pure CO_2[18] under our experimental conditions. This fact was supported by the observation of a single phase for all the CO_2 experiments conducted in this study.

Peak Assignment. FT-IR spectra for different crown ether concentrations (0−0.25 mol L^{-1}) and a fixed D_2O concentration (0.049 mol L^{-1}) are shown in parts a and b of Figure 2 for liquid and SF-CO_2, respectively. Peaks for the free D_2O, i.e., D_2O dissolved in SF-CO_2 without the crown ether (O−D stretching, asymmetric at 2761 cm^{-1} and symmetric at 2654 cm^{-1}), can be easily discerned, and their positions are in agreement with those reported for D_2O molecules in the vapor (i.e., 2789 and 2666 cm^{-1} for the D_2O vapor).[19] The shifts of the D_2O vibrational stretchings to lower wavenumbers in SF-CO_2 relative to those of single molecules in the vapor phase reflect the interactions of D_2O molecules with CO_2 in the fluid phase. When 18-crown-6 was added to the CO_2 solution, three other peaks at 2733, 2679, and 2590 cm^{-1} appeared. According to the order of peak assignment of H_2O−18-crown-6 complex in carbon tetrachloride,[12] the broad peak at 2590 cm^{-1} should correspond to the symmetrical stretch of the O−D bond involved in the two-hydrogen-bond bridge as illustrated in Figure 1a. The D_2O molecule with one hydrogen bond to the cavity oxygen is expected to have two stretching bands. The sharp O−D band at 2733 cm^{-1} should be the unbonded O−D stretching marked as 2 in Figure 1b. The bonded O−D stretching band (marked as 1 in Figure 1b) was assigned to the 2679 cm^{-1} peak, located between the symmetrical and the asymmetrical stretching bands of free water. In the FT-IR spectra of the H_2O−18-crown-6 complex in CCl_4, the bonded O−H stretching band was found at a lower energy than the symmetrical stretch band of free water. We confirmed our assignment of this bonded O−D band by completing two secondary experiments. One experiment was a comparison of the FTIR spectra of 18-crown-6−H_2O and 18-crown-6−D_2O complexes in CCl_4. We confirmed the peak assignment of the former as reported in the literature, and the D_2O isotopic effect altered the peak order of the latter as shown in Figure 2. In another experiment, we confirmed that the order and assignment of the various O−D bands in the 18-crown-6−D_2O complex in SF-CO_2 were the same in both CCl_4 and liquid CO_2.

We also obtained the FT-IR spectra of methanol-*d* mixed with the crown ether in supercritical CO_2 (Figure 3a). The peaks between 2860 and 3100 cm^{-1} correspond to the stretching of the C−H bonds belonging to the methanol-*d* molecule. Due to a different O−D bond energy for methanol-*d* vs D_2O, the peak maximum of the O−D stretching mode for methanol-*d* is shifted

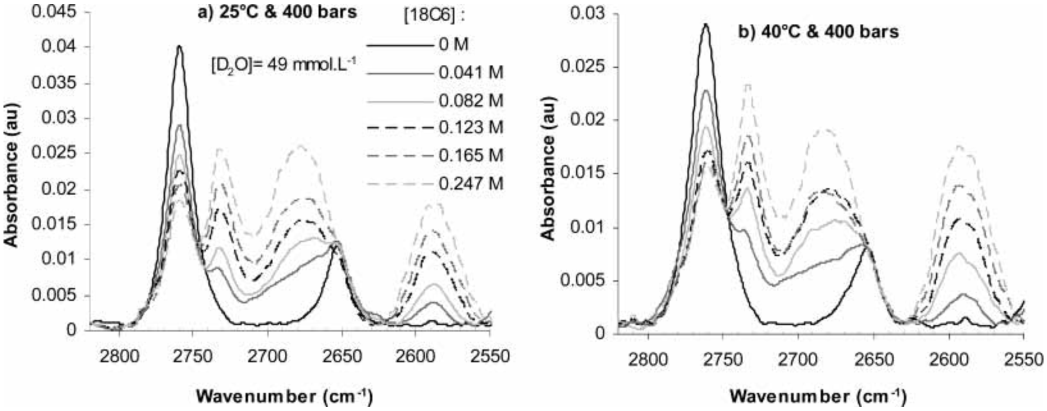

Figure 2. FT-IR spectra of free and bonded D_2O at different 18-crown-6 concentrations (0−0.25 mol L^{-1}) and at one fixed D_2O concentration (0.049 mol L^{-1}) in liquid (a, 25 °C and 400 bar) and supercritical (b, 40 °C and 400 bar) CO_2.

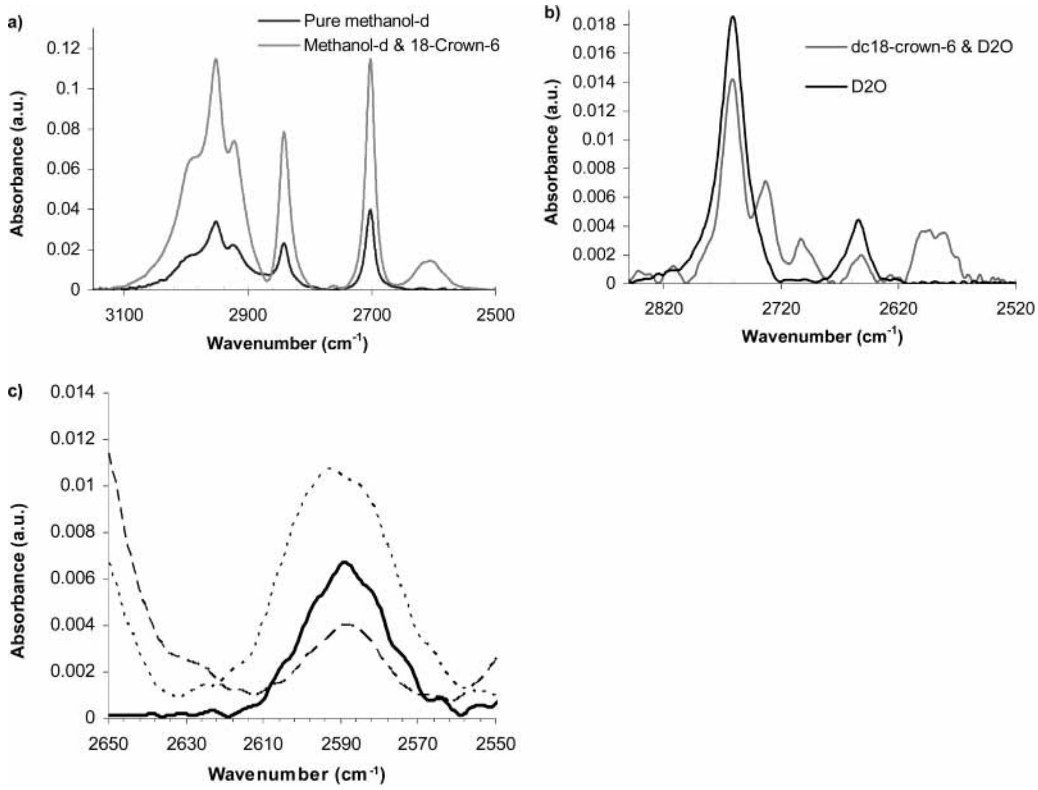

Figure 3. (a) Free methanol-*d* (0.17 mol L^{-1}) and methanol-*d* (0.17 mol L^{-1}) complexed to 18-crown-6 (0.02 mol L^{-1}) in CO_2 (40 °C and 200 bar). (b) Free D_2O (49 mmol L^{-1}) and D_2O (49 mmol L^{-1}) complexed to dicyclo-18-crown-6 (0.06 mol L^{-1}) in CO_2 (40 °C and 300 bar). (c) D_2O (respectively 17 and 49 mmol L^{-1}) complexed to 18-crown-6 (respectively at 0.40 mol L^{-1} (—), 0.041 (− − −), and 0.123 (---) mol L^{-1}) in CO_2 at, respectively, 40 °C and 200 bar and 40 °C and 400 bar.

to a higher energy. Nevertheless, both asymmetric and symmetric free O−D stretching peaks (respectively at 2841 and 2701 cm^{-1}) were observed in the spectra shown in Figure 3a. Moreover, only the bonded O−D stretching band (similar to 1 in Figure 1b) appeared at the expected position (i.e., 2609 cm^{-1}). These observations provided further support for our peak assignment.

Recent molecular dynamic simulation studies performed by Wipff et al.[20] for 18-crown-6 and water in SF-CO_2 suggest that most of the water molecules were bridge bonded to crown ether in the D_{3d} conformation. The observation of a singly bonded water to a crown complex in our experiments could be due to the flexibility of the macrocyclic molecule; 18-crown-6 can be in various conformations that may favor a singly or a doubly bonded water molecule. The 18-crown-6 cavity in dicyclohexano-18-crown-6 is forced by its geometry into the D_{3d} conformation and is supposed to be rigid. The FT-IR spectra of D_2O with and without dicyclohexano-18-crown-6 in SF-CO_2 are shown in Figure 3b. The spectrum shows that the free D_2O stretching bands are observed at 2761 (asymmetric) and 2653 (symmetric) cm^{-1}. For the D_2O with crown solution both single hydrogen bonding (at 2701 (bonded) and 2732 (unbonded) cm^{-1}) and double hydrogen bonding (at 2591 cm^{-1}) with the oxygen atoms of the macrocyclic cavity, similar to that found in 18-crown-6, are observed. The difference between our spectroscopic study and Wipff's molecular dynamic simulation may be due to differences in species concentrations and CO_2 densities used in the simulation study.

TABLE 1: Apparent Molar Absorptivity at Different CO_2 Densities[a]

pressure (bar)	199	199	200	199	200	200	199	199	301	352	403	403
temperature (°C)	70	60	50	40	35	33	31	25	40	40	40	25
density (g mL^{-1})	0.659	0.723	0.784	0.840	0.860	0.870	0.888	0.914	0.911	0.930	0.957	1.035
ϵ_1 (L mol^{-1} cm^{-1})	10	11	13	16	17	18	20	20	18	19	20	24
ϵ_2 (L mol^{-1} cm^{-1})	45	52	60	68	73	74	80	79	74	78	81	93
ϵ_3 (L mol^{-1} cm^{-1})			42	41	41	42	44	44	39	37	35	39
ϵ_4 (L mol^{-1} cm^{-1})	527	517	504	489	484	480	477	469	481	482	481	463
ϵ_5 (L mol^{-1} cm^{-1})	296	288	278	269	264	262	260	254	266	268	268	255

[a] ϵ_1, free D_2O asymmetric (2761 cm^{-1}) stretching band; ϵ_2, free D_2O symmetric (2654 cm^{-1}) stretching band; ϵ_3, doubly bonded D_2O to crown band (at 2593 cm^{-1}); ϵ_4 and ϵ_5, C−H stretch band of 18-crown-6 at 2872 and 2947 cm^{-1}, respectely.

1:2 Complex Formation. When the 18-crown-6 concentration exceeds 0.4 mol L^{-1} with a lower water concentration (less than 17 mmol L^{-1}), only one absorption band at 2590 cm^{-1} is observed (Figure 3c). All the D_2O molecules seem to be bridge bonded to the crown ether. This observation may be explained by the formation of a 1:2 complex between D_2O and 18-crown-6 as illustrated in Figure 1c. The O−D stretching band for this kind of complex should appear at the same frequency as that of the bridged form of D_2O (Figure 1a configuration). Our suggestion of 1:2 complex formation is based on the assumption that, by increasing the crown ether to water ratio in SF-CO_2, we do not change the equilibrium between D_2O molecules bonded to one oxygen atom (configuration 1b) or to two oxygen atoms (configuration 1a) of the cavity. As the concentration of 18-crown-6 in the system increases, it is conceivable that the singly bonded D_2O molecule (configuration 1b) would form a hydrogen bond with another crown molecule via the unbonded O−D, thus leading to the formation of a 1:2 complex. The law of mass action should favor the shifting of equilibrium from a 1:1 complex to a 1:2 complex between water and 18-crown-6 in SF-CO_2. Also in Figure 3c, we show, for comparison, spectra of the double bond area of 18-crown-6 (at 0.041 and 0.123 M) and D_2O (0.049 M) at 400 bar and 40 °C. Peaks occur at the same position for both the dimer and the monomer forms.

The sandwich form (configuration 1c) is a probable conformation for the 1:2 complex, but other configurations (e.g., from offset to perpendicular) can be envisaged. Formation of 1:2 complexes has been reported for crown ether extraction of metal ions from aqueous solutions where a metal ion can bind to two crown cavities to form a sandwich complex. We are not aware of any previous report regarding 1:2 complex formation between water and crown molecules. Our experimental data indicate that, with increasing crown to D_2O ratios in the SF-CO_2 system, the intensities of the single-hydrogen-bond D_2O stretching peaks (2733 and 2679 cm^{-1}) decreases and that of the peak at 2590 cm^{-1} increases. Although the 1:2 complex forms at high crown to D_2O ratios, we cannot distinguish the bridging 1:1 complex (configuration 1a) and the 1:2 complex (configuration 1c) from the FT-IR spectra.

Molar Absorptivity Calculation. A number of experimental parameters (e.g., path length change, radiation of the cell, etc.) can influence molar absorptivity values in addition to pressure and temperature effects in SF-CO_2 as reported in the literature.[22] Therefore, for quantitative discussion of FT-IR data, molar absorptivity should be evaluated for each SF-CO_2 condition.[21]

The molar absorptivities for free D_2O dissolved in CO_2 (Table 1 and Figure 4) were determined by the analysis of FT-IR spectra with pure D_2O of known concentrations. The apparent molar absorptivity of D_2O, in liquid and supercritical CO_2, increases with the fluid density. This behavior is similar to that reported for pyrene and anthracene[21] in CO_2 solutions. In our system, the molar absorptivity for the asymmetric stretching band of the free D_2O at 2761 cm^{-1} is more than doubled for an increase in CO_2 density from 0.66 to 1.04 g mL^{-1}. The molar absorptivities of the C−H stretching vibrations of pure 18-crown-6 dissolved in CO_2 at its maximum intensity (2872 cm^{-1}) and at 2947 cm^{-1} are also given in Figure 4. A 20% decrease in molar absorptivity is observed for both wavenumbers when the CO_2 density varies from 0.65 to 1.0 g mL^{-1}. Because of the stability of those C−H stretches, this decrease might reflect changes in molecular absorptivities due to experimental parameters and needs to be considered to determine true molecular absorptivities. Molar absorptivity changes for free D_2O stretching vibrations might be caused by a change in solute−solvent interaction and in solvent refractive index.

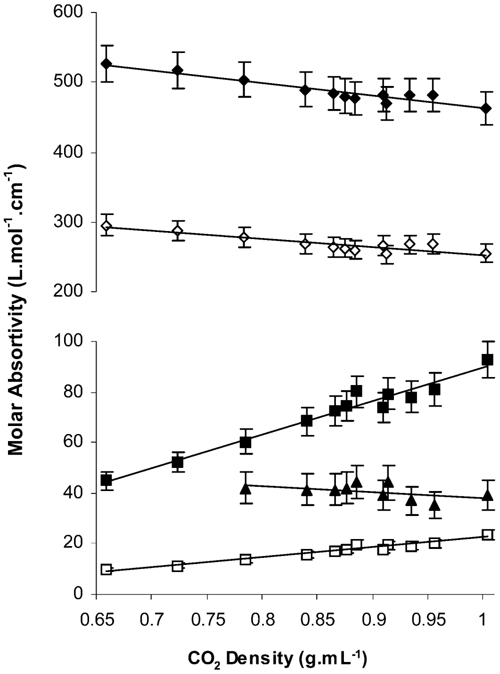

Figure 4. Apparent molar absoptivity at different CO_2 densities: (■) free D_2O asymmetric (ϵ_1 at 2761 cm^{-1}) stretching bands; (□) free D_2O symmetric (ϵ_2 at 2654 cm^{-1}) stretching bands; (▲) doubly bonded D_2O to crown (at 2593 cm^{-1}); (◆, ◇) C−H stretch band of 18-crown-6 at 2872 and 2947 cm^{-1}, respectively.

The molar absorptivity of the bridging 1:1 complex was determined in the following way. We assumed that the molar absorptivities of the 1:1 bridge complex and the 1:2 complex were similar. Thus, the molar absorptivity of the bridged 1:1 complex could be obtained from the region with high 18-crown-6 to D_2O ratios in SF-CO_2. Its value (Table 1 and Figure 4) at 2593 cm^{-1} does not seem to be affected by the change in density. However, the weak solubility limit of 18-crown-6 at low CO_2 density did not permit this calculation for a density below 0.8 g mL^{-1}.

Equilibrium Constants and Enthalpy Calculations. The formation of a 1:1 complex between 18-crown-6 and D_2O in

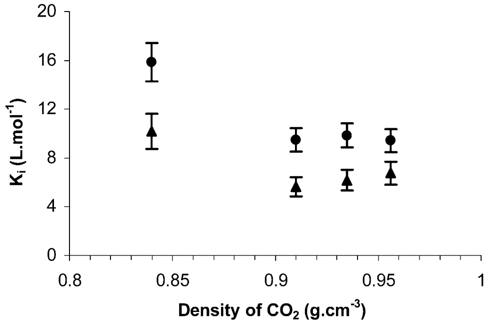

Figure 5. Density effect on equilibrium constants K_s (●) and K_b (▲). The pressure varies from 200 to 400 bar at constant temperature (40 °C). [18C6] = 41 mmol.L^{-1}. [D_2O] = 49 mmol L^{-1}.

the CO_2 phase at a lower crown to D_2O molecular ratio was evaluated by the analysis of the FT-IR data and the equilibrium relations of the following equations:

$$18C6 + D_2O \leftrightarrows 18C6{\cdot}D_2O^{single} \tag{1}$$

$$K_s = ([18C6{\cdot}D_2O^{single}])/([18C6][D_2O])$$

$$18C6 + D_2O \leftrightarrows 18C6{\cdot}D_2O^{bridge} \tag{2}$$

$$K_b = ([18C6{\cdot}D_2O^{bridge}])/([18C6][D_2O])$$

where K_s and K_b represent the equilibrium constants for the 1:1 complex with a single hydrogen bond and double hydrogen bonds, respectively. The total bonded water concentration for equilibrium constant calculations was calculated from the free water concentration (deduct from its molar absortivity) and the total concentration introduced in the cell. The K values vary considerably with CO_2 density. At a constant pressure (200 bar), the K_s value decreases from 21 ± 2 to 13 ± 1 L mol^{-1} with an increase in temperature from 25 to 60 °C. The variation of K_b with temperature is even greater for the same pressure; its value varies from 14 ± 2 to 2 ± 1 L mol^{-1} from 25 to 60 °C. These K values are comparable to the one reported by Moyer et al. (i.e., 15.6(1.2) L mol^{-1}) for the 18-crown-6−H_2O complex in carbon tetrachloride. This implies that, in terms of hydrogen bonding between water and 18-crown-6, liquid CO_2 and supercritical CO_2 behave as nonpolar solvents such as CCl_4 and not chloroform. The K value of the 18-crown-6−H_2O complex in chloroform was reported to be 20 times larger than that in CCl_4.

The influence of density (increase in pressure from 200 to 400 bar) at a constant temperature (i.e., 40 °C) on the two equilibrium constants K_s and K_b is shown in Figure 5. An increase in density causes a decrease in the K_s and K_b values.

The molar enthalpy of a hydrogen bond (ΔH_i) can be determined from the equilibrium constant at constant pressure by eq 4 from well-known thermodynamic relations (eq 3),[17] where T is the absolute temperature in (K) and R the ideal gas constant.

$$\left(\frac{\partial(\Delta G_i)}{\partial T}\right)_P = -\Delta S_i = \frac{\Delta G_i - \Delta H_i}{T} \quad \text{and} \quad \Delta G_i^\circ = -RT\ln K_i \tag{3}$$

$$\left(\frac{\partial(\ln K_i)}{\partial(1/T)}\right)_P = -\frac{\Delta H_i}{R} \tag{4}$$

Using a linear regression on the plot of ln K versus 1/T (Figure 6), and assuming that ΔH is independent of temperature and density, the ΔH_s (for a single hydrogen bond, configuration 1b) was found to be −12 ± 2 kJ mol^{-1} and ΔH_b (for bridge bonding, configuration 1a) to be −38 ± 3 kJ mol^{-1}, both at 200 bar. The complexation process is exothermic as expected for hydrogen bonding, and its value is similar to the literature values for hydrogen-bonding processes in both liquid solvents and supercritical fluids. The facts that the hydrogen-bonding process is exothermic and that the bonded species are more entropically ordered explain the decrease of K values with the increase of temperature.

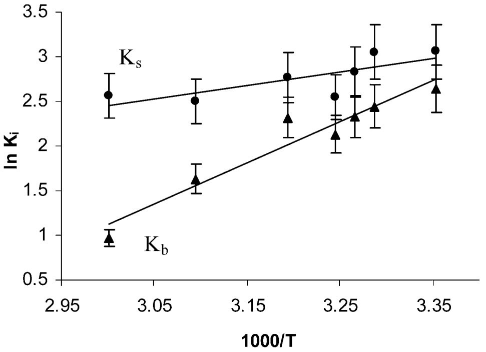

Figure 6. Dependence of ln K_s (●) and ln K_b (▲) on 1000/T at 200 bar for [18C6] = 41 mmol L^{-1} and [D_2O] = 49 mmol L^{-1}.

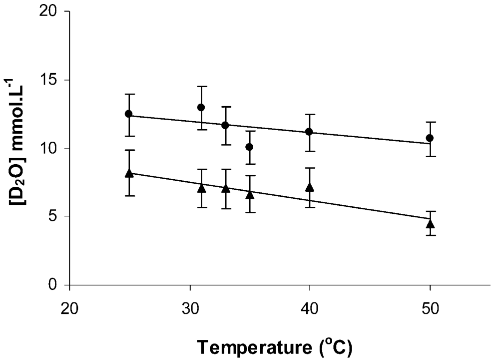

Figure 7. Concentration of the two isomers (i.e., single bond (●) and double bond (▲)) between D_2O (49 mmol L^{-1} total concentration in CO_2) and the 18-crown-6 (83 mmol L^{-1} total concentration in CO_2) versus temperature (°C).

Isomeric Ratio of the Crown−Water Complex. The relative concentrations of the singly bonded and the doubly bonded water−crown complexes change with temperature as shown in Figure 7. At a low crown to water mole ratio (about 0.8), the trend is similar for both isomers. When the temperature is increased from 25 to 50 °C at 200 bar, the concentrations of both the singly bonded and the doubly bonded complexes tend to decrease (Figure 7). The decrease for the doubly bonded complex is perhaps slightly faster than the decrease for the singly bonded complex. This can be explained by an entropy effect; i.e., at higher temperatures the more disordered form should be favored.

At a high crown to water mole ratio (i.e., superior to 1.7), the concentration of the bridged species decreases whereas the concentration of the single-bond species increases when the temperature increases from 25 to 50 °C at a fixed pressure of 200 bar (Figure 8). This observation also appears to support the formation of a 1:2 complex. As expected in terms of entropy, at higher temperatures the 1:2 complex form probably would break down to form a singly bonded 1:1 crown−D_2O complex and unbonded crown ether. Thus, even if the singly bonded species dissociate with rising temperature, the total amount still increases due to the breakdown of the 1:2 complex form.

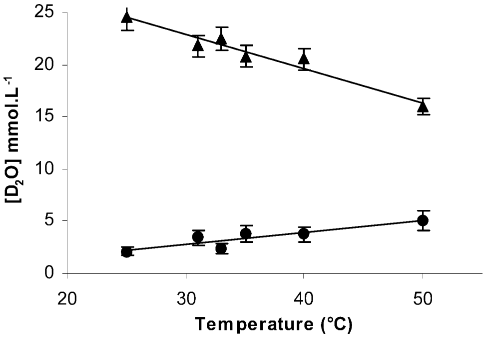

Figure 8. Concentration of the two isomers (i.e., single bond (●) and double bond (▲) between D_2O (49 mmol L^{-1} total concentration in CO_2) and the 18-crown-6 (41 mmol L^{-1} total concentration in CO_2) versus temperature (°C).

Conclusions

FT-IR is a sensitive technique for studying crown ether and water interactions in SF-CO_2. The O−D stretching vibrations for D_2O dissolved in SF-CO_2 show slight shifts to lower wavenumbers relative to those found for D_2O in its vapor phase, indicating interactions (salvation) of CO_2 with D_2O molecules in the supercritical fluid phase. In the presence of 18-crown-6, D_2O forms a 1:1 complex with the macrocyclic molecule with two different configurations. The D_2O molecule can form one hydrogen bond with an oxygen atom of the crown cavity, or it can be bonded to two oxygen atoms of the cavity in a bridged configuration. The equilibrium constant of the single-hydrogen-bond configuration is slightly greater than the two-hydrogen-bond configuration, and both equilibrium constants decrease with increasing temperature. The enthalpy of the complex formation is -12 ± 2 kJ mol^{-1} for the former and -38 ± 3 kJ mol^{-1} for the latter. These values are within the range of hydrogen bonds reported in liquid solvents. At high 18-crown-6 to D_2O ratios, formation of a 1:2 complex in SF-CO_2 that involves one D_2O molecule hydrogen bonded to two crown ether molecules becomes possible.

Acknowledgment. This work was supported by the DOE Office of Environment Management, EMSP Program (Grant No. DE-FG07-98ER 14913). Work by J.L.F. was supported by the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC06-76RLO 1830 with Pacific Northwest National Laboratory.

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