Supercritical Fluids

^{13}C NMR Spectroscopic Evaluation of the Affinity of Carbonyl Compounds for Carbon Dioxide under Supercritical Conditions[**]

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Supercritical carbon dioxide ($scCO_2$) has received much attention as a green alternative to organic solvents for chemical reactions, separations, and extractions because of its pressure-tunable physicochemical properties and economic advantages.[1] A variety of these applications can be realized by controlling the formation of molecular clusters produced by solvation around a solute molecule in $scCO_2$, as well as the mobility of the solute's solvation sphere.[2] The relationships between the solubility and intermolecular interactions of solute molecules in $scCO_2$ have been extensively investigated from the viewpoint of identifying CO_2-philic molecules with a strong affinity for $scCO_2$.[3] It was demonstrated that the solubility of fluorocarbons in $scCO_2$ is exceptionally enhanced by specific interactions of CO_2 with fluorine and/or highly repulsive fluorine–fluorine interactions.[4] Additionally, carbonyl compounds have recently become of interest as inexpensive and easily available CO_2-philes compared to fluorocarbons.[5] For example, spectroscopic and theoretical studies on the interaction of aldehydes, ketones, or acetates in the CO_2 medium suggested that the Lewis acid–Lewis base (LA–LB) interactions between the CO_2 carbon atom and the carbonyl oxygen atoms of these carbonyl compounds play a significant role in the enhancement of CO_2-philicity.[6] In addition to the LA–LB interactions (C=O···C), a relatively weak C−H···O hydrogen-bonding interaction between hydrogen atoms attached to the carbonyl carbon atoms or to the α-carbon atoms and the CO_2 oxygen atoms may also act cooperatively. Most physicochemical studies concerning solute–solvent interactions in $scCO_2$ have focused on the behavior of solute molecules,[3–7] and limited information is available on how the local interactions of CO_2 with solute molecules dissolved in $scCO_2$ affect the bulk properties of the CO_2 solvent. Herein, we discuss the density dependence of the ^{13}C NMR chemical shift (δ_C) of neat CO_2 and CO_2 containing carbonyl compounds under supercritical conditions, and demonstrate the usefulness of the δ_C values of the CO_2 solvent as a reliable criterion for predicting the affinity of solute molecules for $scCO_2$.

The chemical shift δ_C is generally related to the nuclear shielding (σ) arising from intermolecular interactions, and is expressed as a function of the density of the medium ρ ($g\,cm^{-3}$): $-\delta_C \cong \rho\sigma$.[4b,c] We first determined the δ_C values of neat $scCO_2$ in the pressure range 7 to 25 MPa at 40 °C ($0.2 < \rho < 0.9$) using high-pressure NMR spectroscopy as a powerful tool for studying solute–solvent interactions.[8] Figure 1 shows a plot of the δ_C values of neat $scCO_2$ against the density of CO_2. In the higher-density regions ($0.6 < \rho < 0.9$) corresponding to the pressure range 10 to 25 MPa, the δ_C value moves linearly to a higher field with increasing density of CO_2. The slope in Figure 1 is $-1.93 \times 10^{-6}\ cm^3 g^{-1}$, which agrees with the value ($-1.98 \times 10^{-6}\ cm^3 g^{-1}$) expected from a change of only the bulk susceptibility of CO_2. However, the deviation from the linear slope toward the higher field (solid line in Figure 1) was observed in lower-density regions ($0.2 < \rho \leq 0.6$). The appreciable deviation is possibly attributable to the local density enhancement of CO_2, as a result of specific CO_2–CO_2 interactions in the vicinity of the critical density ($\rho_c = 0.469\ g\,cm^{-3}$), as previously published.[9]

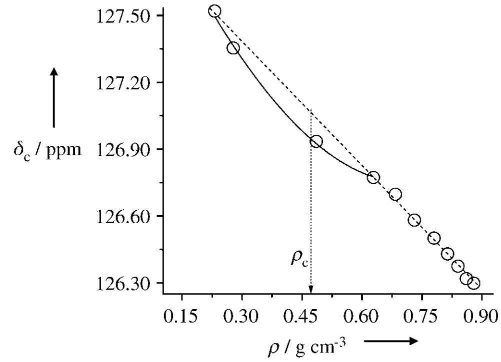

Figure 1. Plot of the δ_C value of neat $scCO_2$ (○) versus the density of CO_2 ($0.2 < \rho < 0.9$). The broken and solid lines are the slope expected from the bulk susceptibility of CO_2 (-1.98×10^{-6}) and experimental data, respectively.

To determine relative CO_2-philicities on the basis of the specific solute–CO_2 interactions, a series of ^{13}C NMR spectra of $scCO_2$ in the presence of β-diketones including acetylacetone (Hacac), 1,1,1-trifluoroacetylacetone (Htfacac), and 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfacac) was measured in the higher-density region above $0.6\ g\,cm^{-1}$. These β-diketones are well-known CO_2-philes for extracting metal ions in $scCO_2$ from industrial radioactive wastes.[2b,10] Figure 2 shows the δ_C values for neat $scCO_2$ and $scCO_2$ containing β-diketones at a concentration of 2.13×10^{-2} M as functions of CO_2 density. The slopes of the linear plots for $scCO_2$ containing Hacac, Htfacac, and Hhfacac were -1.97×10^{-6}, -1.87×10^{-6}, and $-1.92 \times 10^{-6}\ cm^3 g^{-1}$, respectively, which

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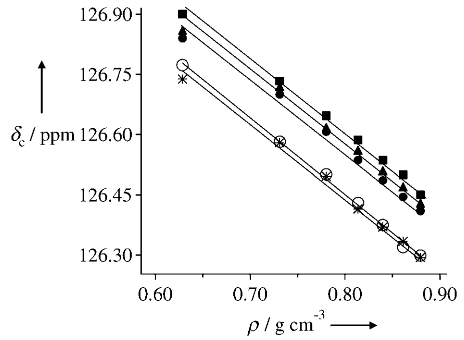
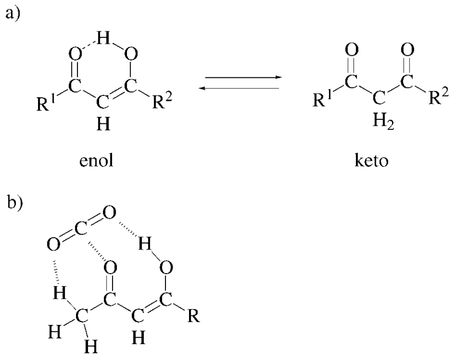


Figure 2. Plots of the δ_c value of neat scCO$_2$ (○) and scCO$_2$ containing Hacac (●), Htfacac (■), Hhfacac (▲), and the [UO$_2$(tfacac)$_2$]·DMSO complex (⁎) versus the density of CO$_2$. The sample concentrations were 2.13×10^{-2} M .

indicates that the δ_C values of these scCO$_2$ systems are also dominated mainly by the bulk susceptibility of CO$_2$.

It is worth noting that the δ_C values of scCO$_2$ containing β-diketones move to lower fields in parallel with the δ_C values of neat scCO$_2$. The magnitude of the parallel shifts ($\Delta\delta_C$) of scCO$_2$ containing these β-diketones decreased in the order Htfacac > Hhfacac > Hacac. The ^{1}H NMR spectra of the β-diketones in scCO$_2$ showed that the enol–keto equilibrium (Scheme 1 a) shifts in favor of enol formation. However, the fraction of the enol isomer of Hacac in scCO$_2$ is about 30 %, which is less than that of Htfacac and Hhfacac in scCO$_2$ (25 MPa, 40 °C).[11,12] Consequently, favorable enol formation should cause an increase in the O–H···O hydrogen-bonding interaction between enolic protons on the β-diketones and the oxygen atoms of CO$_2$.



Scheme 1. a) Tautomeric equilibrium between the enol and keto forms of β-diketones (Hacac: R^1 = CH$_3$, R^2 = CH$_3$; Htfacac: R^1 = CH$_3$, R^2 = CF$_3$; Hfacac: R^1 = CF$_3$, R^2 = CF$_3$). b) Schematic structures showing LA–LB interactions and hydrogen bonding between CO$_2$ and β-diketones.

The generation of enhanced electron deficiency at the central carbon atoms of CO$_2$, possibly as a consequence of O–H···O hydrogen bonding, could result in parallel shifts of the δ_C values for scCO$_2$ to a lower-field direction. In addition, the parallel shift might partly arise from the LA–LB interactions between electronically positive carbon atoms of the CO$_2$ molecules and negative carbonyl oxygen atoms of the β-diketones as well as C–H···O hydrogen bonding between terminal CH$_3$ protons of the β-diketones and the CO$_2$ oxygen atoms, as previously proposed by Wallen and co-workers(see Scheme 1 b).[6] The decrease in $\Delta\delta_C$ values induced by Hhfacac is attributable to the lack of protons participating in the C–H···O interactions. As shown in Figure 3, the $\Delta\delta_C$ value of scCO$_2$ containing Htfacac in the lower-field direction was markedly increased with increasing concentration of Htfacac.[13] Thus, an enhancement of the CO$_2$–solute interactions through the LA–LB and/or hydrogen-bonding interactions reflects an appreciable gain of the parallel shifts of the δ_C values of CO$_2$.

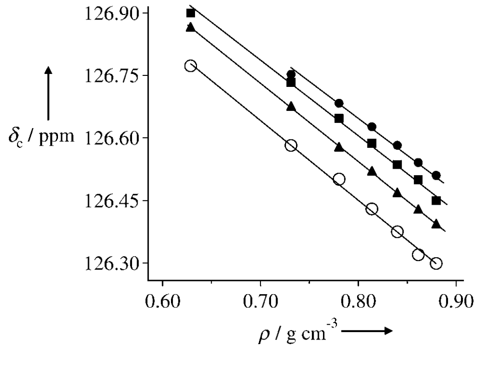
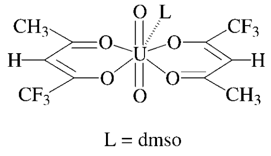


Figure 3. Plots of the δ_C values of neat scCO$_2$ (○) and scCO$_2$ containing Htfacac versus the density of CO$_2$, and the dependence of the δ_c values on the concentration of Hfacac. The sample concentrations were 2.00×10^{-3} M (▲), 2.13×10^{-2} M (■), and 1.20×10^{-1} M (●).

The validity of the parallel shifts of the δ_C values based on the CO$_2$–solute interactions can be demonstrated by a separate experiment using the [UO$_2$(tfacac)$_2$]·DMSO complex[14] (tfacac = 1,1,1-trifluoroacetylacetonato, DMSO = dimethyl sulfoxide) in scCO$_2$ (Scheme 2). Figure 2 shows that the [UO$_2$(tfacac)$_2$]·DMSO complex does not provide any significant parallel shifts from the result obtained with neat CO$_2$, because the absence of free carbonyl and OH groups in the coordinating tfacac moiety prevents it from strongly affecting the CO$_2$ solvent properties.



Scheme 2. Schematic structure of the [UO$_2$(tfacac)$_2$]·DMSO complex.

The $\Delta\delta_C$ values of CO$_2$ containing organic compounds can be used for assessment of the relative CO$_2$-philicities of solute molecules in scCO$_2$. Table 1 shows the $\Delta\delta_C$ values of scCO$_2$ containing CH$_3$OH, (CH$_3$)$_2$CO, HCON(CH$_3$)$_2$, CH$_3$CHO, and (CH$_3$)$_2$SO (2.25×10^{-2} M), estimated from the density dependence of the δ_C values in a similar manner as scCO$_2$ containing β-diketones. The $\Delta\delta_C$ values for CO$_2$ doped with these compounds are apparently smaller than those of β-diketones

Table 1: Slopes of the linear plots (σ) and the parallel shift ($\Delta\delta_C$) values of neat $scCO_2$ and $scCO_2$ containing organic solute molecules.[a]

Solute	σ ($cm^3 g^{-1}$)	δ' (at 0.6 $g cm^{-3}$)	$\Delta\delta_C$
neat $scCO_2$	-1.93×10^{-6}	126.828	–
Htfacac[b]	-1.87×10^{-6}	126.988	0.160
CH_3OH	-1.89×10^{-6}	126.926	0.098
$(CH_3)_2CO$	-1.92×10^{-6}	126.918	0.090
$HCON(CH_3)_2$	-1.87×10^{-6}	126.898	0.070
CH_3CHO	-1.91×10^{-6}	126.884	0.056
$(CH_3)_2SO$	-1.84×10^{-6}	126.906	0.078

[a] The δ' values are the chemical shifts of CO_2 at 0.6 $g cm^{-3}$ calculated from experimental data using the least-squares method, and the $\Delta\delta_C$ values are the differences of the δ' values between the neat $scCO_2$ and $scCO_2$ containing organic solutes. [b] For comparison, the $\Delta\delta_C$ value of $scCO_2$ containing Htfacac (☆, Figure 2) is also shown.

and decrease in the order $CH_3OH > (CH_3)_2CO > (CH_3)_2SO > HCON(CH_3)_2 > CH_3CHO$. Thus, the CO_2 solvent properties might be strongly perturbed by alcoholic protons through the O–H···O hydrogen-bonding interaction, rather than by carbonyl oxygen atoms and neighboring hydrogen atoms through the LA–LB interaction (C=O···C) and the cooperative C–H···O hydrogen-bonding interaction. The latter effect should give rise to increasing $\Delta\delta_C$ values in $(CH_3)_2CO$ and $HCON(CH_3)_2$ compared with that in CH_3CHO, because of an increase in the number of C–H···O hydrogen bonding sites. The difference in the $\Delta\delta_C$ values between $(CH_3)_2CO$ and $HCON(CH_3)_2$ could be interpreted as resulting from the symmetrical structure of acetone, which leads to less steric hindrance and allows the CH_3 protons to move closer to the CO_2 oxygen atoms. Moreover, the sulfinyl moiety is also available as a CO_2-philic functional group, possibly as a result of an LA–LB interaction (S=O···C) of the sulfinyl groups[6a] as well as the C–H···O hydrogen-bonding interaction.

In summary, we have demonstrated the density dependence of δ_C values of neat $scCO_2$ and $scCO_2$ containing solute molecules, which clearly provide a useful and reliable criterion for evaluating the CO_2-philicity of solutes in $scCO_2$. A marked correlation between the parallel shifts, $\Delta\delta_C$, of $scCO_2$ and the structures of the solute molecules is attributed to LA–LB interactions and/or hydrogen-bonding interactions between the solute and CO_2 molecules. Such reproducible parallel shifts are based on the fact that the local CO_2–solute interactions influence a large number of CO_2 molecules under supercritical conditions. The use of ^{13}C NMR spectroscopy to obtain novel information about $scCO_2$ could be a viable approach to designing CO_2-philic materials and could lead to the development of polymers, cosolvents, catalysts, surfactants, and chelating agents.

Experimental Section

^{13}C NMR spectra were measured using a JEOL JNM-LA300 spectrometer at 75.5 MHz and 40 °C in the pressure range 7 or 10 to 25 MPa without spinning. A zirconia cell (inner diameter 5.4 mm, outer diameter 9.0 mm, length 152.0 mm) was used as a high-pressure NMR cell, which enabled measurements at up to approximately 50 MPa. A glass capillary containing C_6D_6 as an internal lock was inserted into the high-pressure cell. This tube was effective for easily adjusting the shim coil and for minimizing the sample's convection. The reproducibility of all chemical shifts was better than ±0.005 ppm, and the susceptibility of the C_6D_6 in the capillary was constant. The δ_C values were referenced to the carbon atoms at 128.0 ppm in the C_6D_6. The effective sample volume was 0.8 cm^3. The zirconia cell was mounted in a stainless-steel sample holder and sealed with a stainless-steel valve and an O-ring. Pressure was exerted on the NMR cell with an ISCO syringe pump by charging it with CO_2 gas, and monitored by a back-pressure regulator (JASCO, 880-81). Impurities and air in the stainless-steel tube, which was connected to the high-pressure NMR cell, were removed by evacuating the cell several times. The temperature of the samples was controlled by supplying heated air with a temperature control unit in the NMR spectrometer. The high-pressure NMR apparatus used in the present study was described in more detail previously.[15]

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[13] In Figure 3, the δ_C values of $scCO_2$ containing 1.20×10^{-1} M Htfacac at around 0.60 $g\,cm^{-3}$ were not plotted because of insufficient solubility of Htfacac in $scCO_2$.

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