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ARTICLES

Solution Dynamics of Perfluorobenzene, Benzene, and Perdeuteriobenzene in Carbon Dioxide as a Function of Pressure and Temperature

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The ^{19}F, ^{1}H, and ^{2}H relaxation times of perfluorobenzene, benzene, and perdeuteriobenzene were measured in carbon dioxide using capillary high-pressure NMR spectroscopy. The pressure range for the measurement of the ^{19}F, ^{1}H, and ^{2}H nuclear relaxation times was between 400 and 2300 atm over a temperature range of 298−423 K. The density regime of the solvent, carbon dioxide, over these conditions was between 0.55 and 1.27 g/cm^3. Over this wide range of solvent conditions, the contributions to the molecular relaxation processes for both ^{1}H and ^{19}F in CO_2 were determined. These conditions were chosen to address the occurrence of specific molecular interactions between CO_2 and fluorine. From the comparison of the relaxation processes for ^{19}F and ^{1}H in CO_2, especially at high densities, any interaction between fluorine and carbon dioxide should be prevalent. No specific interaction between fluorine and CO_2 contributing to the molecular relaxation of these nuclei was noted over the temperature and pressure range investigated in this study.

Introduction

The interaction between fluorine and supercritical CO_2 has been under speculation since the determination of enhanced solubility of fluorinated compounds in this solvent.[1] Yee, Fulton, and Smith[2] studied the intermolecular interactions between supercritical CO_2, ethane, and perfluoroethane by infrared spectroscopy. They reported no specific intermolecular interaction between CO_2 and fluorine over the range of conditions investigated. The change in the observed frequency shifts of the ν_2 bending mode of CO_2 in perfluoroethane and ethane led to the postulate that CO_2 is more repulsive to perfluoroethane than ethane. They concluded that the enhanced solubility of fluorinated compounds in CO_2 was due to the highly repulsive fluorocarbon/fluorocarbon interaction, which favors solute/solvent interactions over solute/solute interactions. In 1996, Hartree−Fock calculations were performed by Cece et al.[3] in which a favorable interaction energy of 0.75−0.80 kcal/mol for each CO_2 molecule in the first solvent shell was reported. Their calculations showed a clustering of CO_2 molecules around C_2F_6, with the positively charged CO_2 intercalated between the two negatively charged fluorine atoms; there was minimal interaction between CO_2 and the hydrocarbon molecules. These computations purportedly identified differences between the interaction of hydrocarbon and fluorocarbon molecules with CO_2, which could help explain the solubility differences for these molecular classes in supercritical CO_2. A comment on these calculations by Han and Jeong[4] brought into question the use of a restricted Hartree−Fock level of calculation. They demonstrated that with the use of basis-set superposition error (BSSE) correction in the calculation there was no binding between the two sets of molecules. Recently, Diep et al.[5] revisited the Hartree−Fock calculation of the interaction between CO_2 and small fluorocarbons and hydrocarbons. They concluded that Hartree−Fock calculations, using flexible basis sets, failed to demonstrate appreciable binding for the geometries studied. Using MPS methods (many-body perturbation theory) with flexible basis sets and corrections for BSSE gave binding energies ranging from −0.79 to −1.17 kcal/mol for the cluster geometries investigated. They reported slightly larger binding energies for the CO_2/hydrocarbon complex than for the CO_2/perfluorocarbon complex. This is in direct contrast to the earlier work of Cece et al.[3] Dardin, DeSimone, and Samulski[6] investigated the proton and fluorine NMR chemical shifts of *n*-hexane and perfluoro-*n*-hexane in CO_2 as a function of pressure and temperature. They studied the nuclear shielding difference between the two molecules taking into account the change in bulk magnetic susceptibility of the CO_2 solvent with density. On the basis of their investigations, they concluded that the excess nuclear shielding effects determined in the ^{19}F studies, as compared to the bulk magnetic susceptibility dominated ^{1}H NMR findings, demonstrated specific intermolecular interactions between CO_2 and fluorine.

NMR relaxation measurements provide information about the rotational reorientation and spatial reorientation (translational motion) of molecules in solution. The relaxation rate of pure perfluorobenzene has been reported as a function of temperature from 253 K to above the critical temperature of 516.7 K.[7] Asahi and Nakamura[8] have recently reported the relaxation times and self-diffusion coefficients for liquid and supercritical benzene at four densities: 0.101, 0.154, 0.250, and 0.302 g/cm^3 over a temperature range of 298−650 K. Kobayashi et al.[9] and Lüdemann et al.[10] have reported the relaxation times and the self-diffusion coefficients for carbon dioxide as a function of pressure and temperature (223−450K and 10−2000 bar). To

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date, there have been no reported relaxation studies of CO_2 solutions of hydrocarbons and fluorocarbons that could reveal some important insights into the question of specific CO_2/F interactions.

In this study, measurement of the T_1 values of perfluorobenzene, benzene, and perdeuteriobenzene in CO_2 as a function of pressure and temperature is investigated to address the role of potential CO_2/F intermolecular interactions in solution. The perfluorobenzene molecule has a C_6 6-fold symmetry axis for in-plane rotation and a C_2 symmetry axis of tumbling about the molecular plane. While it was impossible in this investigation to determine the difference between the two types of molecular motion, specific interactions between CO_2/F would be anticipated to impact on the molecular rotational reorientation as determined by T_1 measurements. The pressure range for both the ^{19}F and ^{1}H nuclear relaxation rates in solution is between 400 and 2300 atm over a temperature range of 298−423 K. The density range of the solvent, carbon dioxide, over these conditions was between 0.55 and 1.27 g/cm^3. These investigations should probe any potential CO_2/F interaction over a wide range of temperatures, pressures, and density.

Experimental Section

Perfluorobenzene, perdeuteriobenzene, and benzene (Aldrich Chemical Co.) were freeze−pumped−thawed and loaded into a high-pressure extraction vessel maintained under an inert atmosphere. The extraction vessel was then attached to a high-pressure syringe pump and connected to the high-pressure fused silica capillary NMR cell. The capillary was 100 μm i.d. by 360 μm o.d. The experimental setup and high-pressure pump have been described previously.[11,12] The whole experimental system was evacuated before filling with CO_2. The capillary NMR cell was filled from the extraction vessel containing perfluorobenzene, perdeuteriobenzene, or benzene in equilibrium with liquid CO_2 at room temperature. The mole fraction of the solute in the CO_2 solution was ∼0.10 for the three molecules investigated. The solution in the extraction vessel was then transported into the capillary NMR cell by opening a high-pressure valve at the end of the capillary. Once the capillary was filled from the extraction cell, the extraction cell was isolated from the system and the high-pressure pump. A hand-operated high-pressure syringe pump (HIP, Inc.) was then used to adjust the CO_2 solution pressure in the high-pressure capillary NMR cell. A standard inversion recovery pulse sequence ($4T_1-180°-\tau-90°$) was used to measure the spin−lattice relaxation times. The 90° pulses were 22.3, 26.5, and 23.2 μs for ^{1}H, ^{2}H, and ^{19}F, respectively. The T_1 values were determined from a nonlinear least-squares fit to the exponential magnetization recovery. The relative reproducibility of the measurement was ∼5−8% for the ^{1}H, ^{2}H, and ^{19}F nuclei. All spectra were acquired on a Varian (VXR-300) 300 MHz pulsed NMR spectrometer with a 7.04 T superconducting magnet. A spectral resolution between 2 and 4 Hz was maintained over the pressure and temperature range studied. Pressure was measured using a calibrated pressure transducer (Precise Sensors, Inc.) with a precision of ±0.7 atm. Temperature was controlled to ±0.1 K using the air bath controller on the NMR spectrometer.

Results and Discussion

Spin−lattice relaxation of a molecule is governed by its interactions with the surrounding solvent bath through complex processes, some of which are composed of internal reorientation, spatial translation, and changes in angular momentum. The spin−lattice relaxation rate (R_{total}) can be described as being composed of contributions from the various relaxation times (T_1) due to dipole/dipole interactions (DD), spin−rotation interactions (SR), quadrupolar interactions (Q), chemical shift anisotropy (CSA), and scalar coupling (SC).

$$R_{\text{total}} = 1/T_1^{\text{total}} = 1/T_1^{\text{DD}} + 1/T_1^{\text{SR}} + 1/T_1^{\text{Q}} + 1/T_1^{\text{CSA}} + 1/T_1^{\text{SC}} \quad (1)$$

These represent the more common nuclear relaxation processes encountered in liquids and gases. These magnetic interactions, DD, SR, CSA, and SC, and magnetic/electric field interactions (Q) will contribute to different degrees in the reequilibration of the nuclei after excitation by the rf field pulse. The goal of this investigation was to study the relaxation of ^{19}F, ^{1}H, and ^{2}H on a standard carbon backbone (benzene) to determine the effect of pressure and temperature on the different relaxation processes and to qualitatively describe any CO_2/F interactions and their effect on molecular relaxation. Any solvent/solute interaction should be similar between CO_2 and benzene, perdeuteriobenzene, or perfluorobenzene—except for any specific CO_2/F interactions. It is hypothesized that T_1 measurements of such solvent/solute combinations at similar pressures and temperatures could distinguish any potential CO_2/F interactions.

The DD relaxation mechanism is a combination of both intramolecular and intermolecular processes. A detailed account of the derivation of T_1 from the various intermolecular and intramolecular dipole/dipole interactions has been described by Bloembergen, Purcell, and Pound.[13] The intramolecular relaxation process is governed by the angular reorientation of the vector connecting the spin $^1/_2$ nuclei—in this case either ^{1}H or ^{19}F in benzene or perfluorobenzene. The relaxation rate is

$$1/T_1(\text{DD-intra}) = (9/10)\gamma_{\text{H}}^{4}\hbar^{2}r_{(\text{H-H})}^{-6}\tau_{\text{c}} \quad (2)$$

γ is the magnetogyric ratio for the proton (or ^{19}F), $\hbar$ is Planck's constant over 2π, $r_{(\text{H-H})}$ is the proton/proton distance in benzene (or fluorine/fluorine distance in perfluorobenzene), and τ_c is the rotational correlation time of the molecule. All these molecules have a C_6 symmetry axis for in-plane rotational orientation and a C_2 symmetry axis of tumbling about the molecular plane. It is impossible from this investigation to determine the difference between these two types of molecular motion. The intermolecular relaxation process has a complex dependence on angular position and spatial reorientation. This has been simplified by expressing the dependence of the relaxation rate in terms of the self-diffusion coefficient (D)

$$1/T_1(\text{DD-inter}) = (3\pi/10)N_0\gamma_{\text{H}}^{4}\hbar^{2}/aD \quad (3)$$

Here N_0 is the number density (number of molecules/cm^3) and a is the distance of closest approach of the nuclei.

The spin−rotation relaxation process becomes important in gases or supercritical fluids at low densities and high temperatures.[11] This relaxation rate is expressed as

$$1/T_1(\text{SR}) = (^2/_3)kT\hbar^{-2}I(2c_{\perp}^{2} + c_{\parallel}^{2})\tau_{\text{J}} \quad (4)$$

where I is the moment of inertia for the molecule, k is Boltzmann's constant, T is temperature, c are the spin−rotation coupling constants, and τ_J is the angular momentum correlation time for the molecule. The spin−rotation relaxation rate is greater for ^{19}F as compared to ^{1}H, because the moment of inertia and the coupling constants are larger for perfluorobenzene.[7] It should be noted that τ_J and τ_c have opposite dependence on temperature; as temperature increases τ_c decreases, whereas, τ_J

increases. The density dependence is also opposite, at high density/low temperatures τ_c is long, and τ_J is short, while for high temperatures/low density, τ_c is short and τ_J long. In fact, for liquids $\tau_J \ll \tau_c$, such that spin−rotation does not play a role in relaxation. These quite different correlation times reflect the difference in molecular motions and dynamics of solution.

The quadrupolar relaxation mechanism is the dominant process for nuclei with spins of $I > {}^1/_2$ such as deuterium (here I is the spin quantum number). Quadrupolar relaxation efficiency is determined by the magnitude of the nuclear quadrupole and the electric field gradient at the nucleus. This interaction is modulated by molecular rotation in a similar manner as for dipole/dipole relaxation. The quadrupolar relaxation rate is

$$1/T_1(\mathrm{Q}) = (3\pi^2/10)(2I + 3/(I^2(2I - 1)))(1 + \eta_s^{\,2}/3)\chi^2\tau_c \quad (5)$$

where η_s is the measure of asymmetry of the quadrupolar nuclei and χ is the nuclear quadrupole coupling constant (which is the product of the electric field gradient and the nuclear quadrupole moment). To determine the quadrupole coupling constant, the free-rotor correlation time was calculated from gas kinetic theory and inserted into eq 5 for τ_c

$$\tau_{(\text{free rotor})} = 2\pi/9(I_\perp/kT)^{1/2} \quad (6)$$

where $I_\perp$ is the perpendicular component of the moment of inertia for the C_6D_6 molecule.[11] The quadrupole coupling constant estimated using the free-rotor correlation time, regressed from the experimental data at 423 K, assuming $\eta_s = 1$, was 202 kHz. Green and Powles reported a value of 172 kHz[7] and Ripmeester et al.[14] reported a value of 184 ± 3 kHz. Our value is reasonable when compared to these reported values. Using the standard expression for T_1 CSA, the chemical shift anisotropy for crystalline C_6F_6 is $\Delta\sigma = 155$ ppm and a rotational correlation time of ~1.0 ps, the relaxation rate was determined to be ~0.000 15 s^{-1}, which can be ignored.[15] The other relaxation process, SC, was assumed to play a negligible role in molecular relaxation for the CO_2 solution.

The experimental relaxation times for benzene and perfluorobenzene in CO_2, as a function of density at the various temperatures investigated, are shown in Figures 1−4. The density of the solution was assumed equal to the CO_2 density for a specific temperature and pressure and was interpolated from reported values.[16] In Figures 1 and 2, the relaxation time for benzene in CO_2 from 303 to 423 K and ~380 to ~2200 atm are plotted against CO_2 density. The general trends in the plot of T_1 for benzene in CO_2 are that at high densities the relaxation times converge for the different temperatures, and overall there is a small temperature effect at constant density (prevalent in the mid-density region) for the reported T_1 values. In Figures 3 and 4, the relaxation time for perfluorobenzene in CO_2 is plotted against CO_2 density over a similar range of temperature and pressure. The trends for perfluorobenzene in CO_2 are similar, at high densities the T_1 values converge and there appears to be a small temperature dependence at constant density in the low-density region.

There have been relaxation time measurements reported in the literature for pure liquid perfluorobenzene and pure liquid benzene at different temperatures, and also at different densities for benzene.[7,8] These studies investigated the T_1 value for the liquid phase of the molecule in the vapor/liquid equilibrium region as a function of temperature below the critical temperature. Asahi and Nakamura[8] report T_1 values for supercritical benzene at low densities. The T_1 values for pure perfluorobenzene and benzene as a function of temperature are shown for the liquid phase in the two-phase region in Figure 5. At low temperatures the T_1 values appear to converge for the two molecules. The variation at higher temperatures is due to the difference in the relaxation mechanism for the two molecules. For benzene, the relaxation mechanism is dominated by DD relaxation at higher temperature, while for perfluorobenzene, the relaxation mechanism is dominated by SR relaxation over this temperature range. As was mentioned above, τ_J and τ_c have opposite dependence on temperature: as temperature increases,

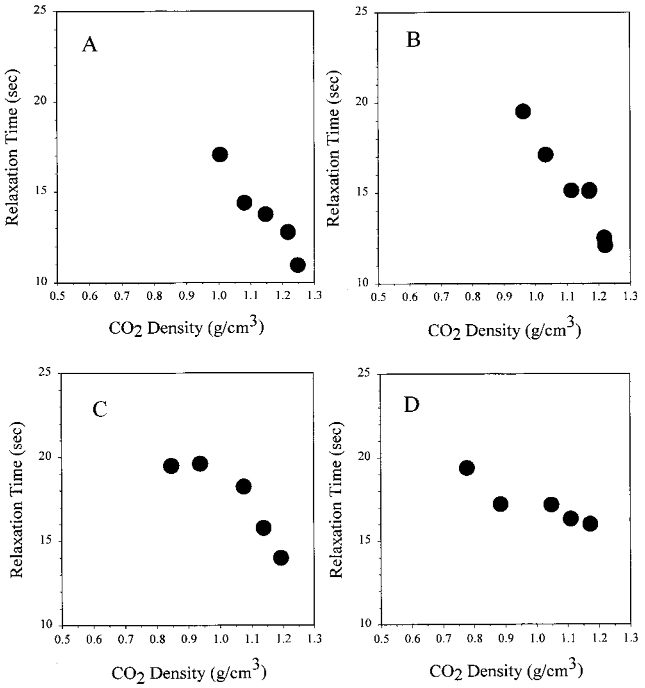

Figure 1. Plot of the relaxation time (T_1) in seconds for benzene in CO_2 versus CO_2 density at the temperatures of (A) 303 K, (B) 323 K, (C) 343 K, and (D) 363 K. The symbol size represents the error for the data.

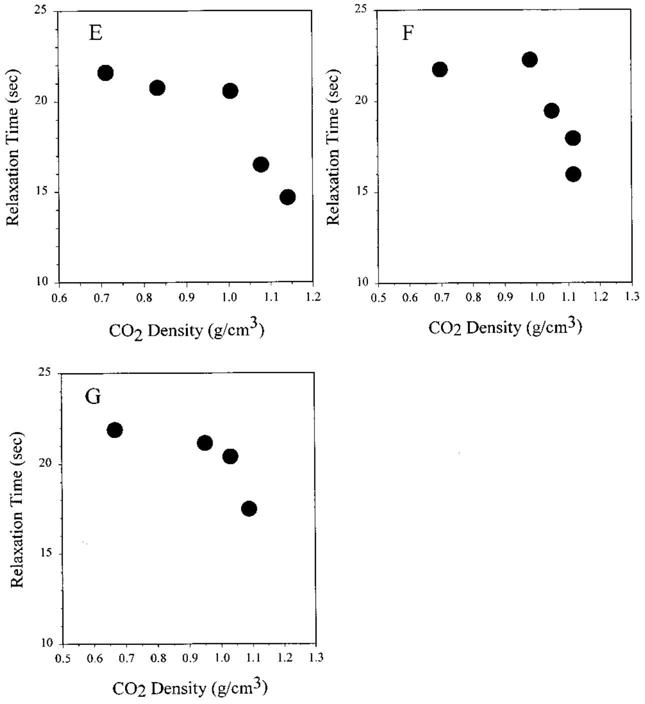

Figure 2. Plot of the relaxation time (T_1) in seconds for benzene in CO_2 versus CO_2 density at the temperatures of (E) 383 K, (F) 403 K, and (G) 423 K. The symbol size represents the error for the data.

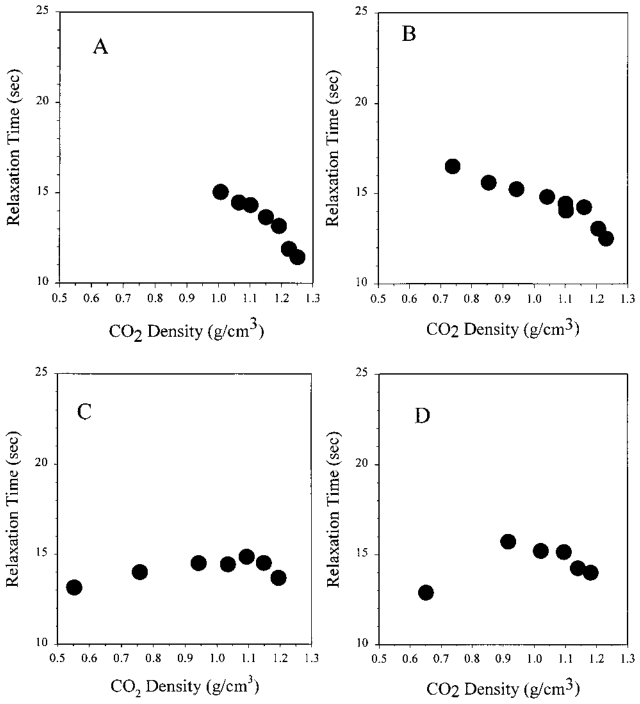

Figure 3. Plot of the relaxation time (T_1) in seconds for perfluorobenzene in CO_2 versus CO_2 density at the temperatures of (A) 297 K, (B) 318 K, (C) 338 K, and (D) 358 K. The symbol size represents the error for the data.

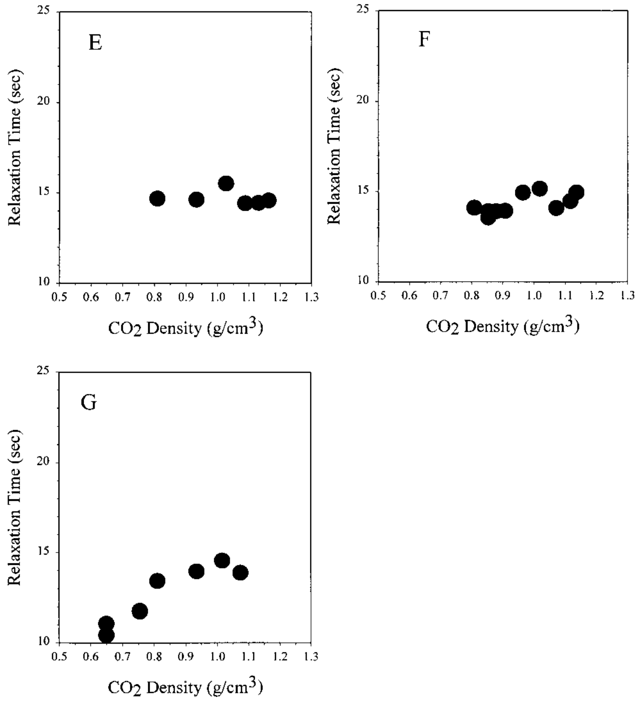

Figure 4. Plot of the relaxation time (T_1) in seconds for perfluorobenzene in CO_2 versus CO_2 density at the temperatures of: (E) 378 K, (F) 398 K, and (G) 423 K. The symbol size represents the error for the data.

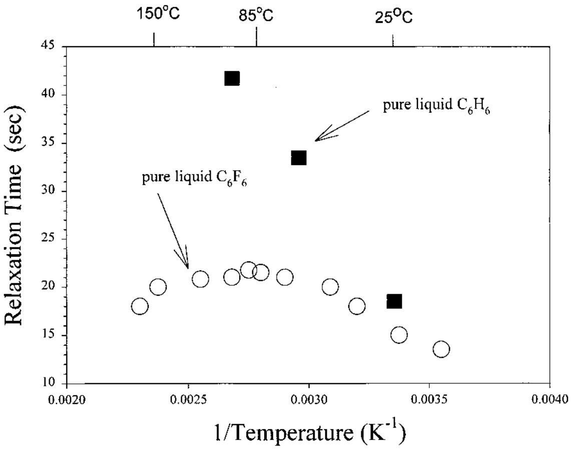

Figure 5. Plot of relaxation time (T_1) in seconds for pure liquid benzene (■) and pure liquid perfluorobenzene (○) as a function of temperature in the two-phase region.[7,8]

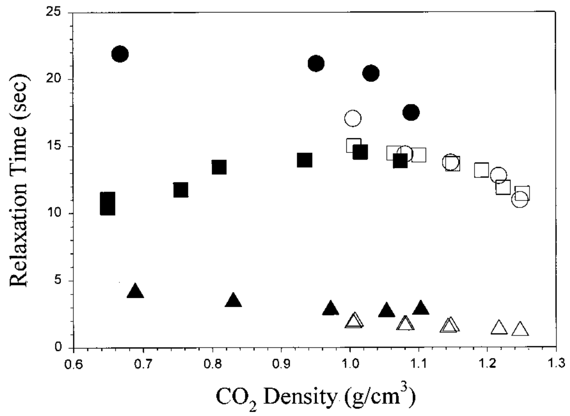

Figure 6. Plot of the relaxation time (T_1) in seconds for benzene in CO_2 (303 K (○) and 423 K (●)), perfluorobenzene in CO_2 (297 K (□) and 423 K (■)), and perdeuteriobenzene in CO_2 (303 K (△) and 423 K (▲)) versus CO_2 density.

τ_c decreases and τ_J increases. This is due to the difference in physical mechanisms: τ_J depends on angular velocity and τ_c depends on angular position. Also one has to consider the larger moment of inertia and the greater spin–rotation coupling constants for the perfluorobenzene molecule (see eq 4) as compared to benzene. Therefore, spin–rotation relaxation is dominant for perfluorobenzene at higher temperatures, while at low temperatures dipole/dipole relaxation is dominant for both benzene and perfluorobenzene. Spin–rotation relaxation does indeed become important for benzene near its critical temperature.[7]

It is interesting to note the absolute difference in the T_1 values reported in Figure 5 and those shown in Figures 1–4. For the CO_2 solvent system, the T_1 values for both C_6H_6 and C_6F_6 are lower than the pure liquids; this is particularly true for benzene. The decrease in T_1 could be due to the solvation interaction between CO_2 and the two solute molecules. Both CO_2 and the two solute molecules have appreciable electric quadrupole moments,[17] which could contribute to a CO_2/benzene or CO_2/perfluorobenzene solution interaction and a faster relaxation time. A more valid comparison between Figure 5 and Figures 1–4 would be under constant density conditions, but the two-phase liquid experiments do not lend themselves to such an analysis.

Figure 6 is a plot of the relaxation time for benzene, perfluorobenzene, and perdeuteriobenzene at the temperature extremes (~303 and 423 K) as a function of CO_2 density. This plot clarifies the behavior seen in Figures 1–4. One can see that at high density the T_1 values for both C_6H_6 and C_6F_6 are the same within experimental error. The T_1 value for C_6D_6 is much smaller than for the other two molecules due to the quadrupole relaxation process. At constant CO_2 density for benzene there is a large temperature effect when compared to C_6D_6 or C_6F_6. The T_1 evidence implies that there is a general interaction for both benzene and perfluorobenzene with CO_2, but there is no suggestion of a specific CO_2/F interaction that perturbs molecular relaxation on the time scale of these experiments. One would anticipate that a specific CO_2/F interaction would be predominant at high CO_2 densities as the packing density increases and the intermolecular distance decreases. But, at the densities investigated both C_6F_6 and C_6H_6 have the same relaxation time in CO_2.

For dipole/dipole relaxation at high densities the increased viscosity would contribute to an increase in the rotational correlation time, τ_c, and a decrease in the diffusion coefficient; both of these factors would contribute to a decrease in T_1(DD). This can be seen from the Debye equation, which relates the viscosity to the rotational correlation time

$$\tau_c = 4\pi a^3\eta/(kT) \tag{7a}$$

and the Stokes−Einstein equation (using a slip assumption equal to 4) which relates viscosity to the diffusion coefficient

$$D = kT/(4\pi a\eta) \tag{7b}$$

where a is the molecular radius and η the viscosity.[9] It is difficult to determine which of the dipole/dipole relaxation mechanisms (intermolecular or intramolecular) is dominant at high densities from an inspection of eqs 7a and 7b. This will be addressed in the next section.

The different relaxation mechanisms can be calculated based on eqs 2−4 using the rotational correlation time, diffusion coefficients, angular momentum correlation time, moments of inertia, and spin−rotation coupling constants for the molecules. From the experimental relaxation times (T_1(Q)) for C_6D_6 in CO_2 over a similar pressure and temperature range as investigated for benzene and perfluorobenzene, one can calculate the rotational correlation time for these conditions using eq 5. Since the quadrupole relaxation process is dependent on the rotational correlation time (angular position), this is the same parameter as in T_1 (DD-intra). Therefore, T_1(DD-intra) can be calculated from eq 2 for both C_6H_6 and C_6F_6 over the pressure and temperature range investigated using the determined χ value of 202 kHz. The self-diffusion coefficients for both CO_2 and benzene have been determined over a narrow range of pressure and temperature.[8−10] These values can serve as a guide in the calculation of T_1(DD-inter) from eq 3, as the benzene molecule should diffuse faster than its self-diffusion coefficient, but slower than the self-diffusion coefficient of CO_2 in solution. The spin−rotation contribution was calculated using the following relationship between the angular momentum correlation time, τ_J, and the rotational correlation time, τ_c[7,9]

$$\tau_c\tau_J = I/(6kT) \tag{8}$$

This relationship is valid only at liquid densities and was assumed valid for the densities studied in this investigation. As shown in Figure 6, the spin−rotation relaxation mechanism appears only in C_6F_6 for the experimental conditions investigated. The rotational correlation time, τ_c, for C_6D_6 was used in eq 8 to determine τ_J for C_6F_6. Therefore, the spin−rotation relaxation time could be calculated using eq 4, from the angular momentum correlation time, the moment of inertia,[18] and the estimated spin−rotation coupling constants based on benzene.[8] The influence of the individual relaxation processes to the overall relaxation mechanism can be calculated and compared with the experimental values.

If one compares the two dominant relaxation processes for benzene in CO_2, T_1(DD-inter) and T_1(DD-intra), under the chosen experimental conditions, looking at eqs 2, 3, and 7a at constant density as temperature increases; D increases, and viscosity decreases. Therefore, at constant density as temperature increases, T_1(DD-inter) would increase and the rotational correlation coefficient would decrease slightly such that T_1(DD-intra) would increase. At constant temperature, as density increases; N_0 increases, D decreases, and viscosity increases, and therefore, T_1(DD-inter) decreases and T_1(DD-intra) decreases. At high densities for all temperatures of benzene in CO_2 investigated, the relaxation time appears to be dominated by T_1(DD-inter) as the diffusion coefficient becomes smaller much more rapidly in the highly compressed solvent than τ_c increases, but T_1(DD-intra) appears dominant for all temperatures at lower densities. Similar behavior is seen for perfluorobenzene in CO_2 at low temperatures. At high temperatures, the spin−rotation relaxation process becomes dominant at low densities and T_1(SR) decreases. At high density for all temperatures investigated, perfluorobenzene's relaxation time appears to be dominated by T_1(DD-inter) as the diffusion coefficient becomes smaller much more rapidly in the highly compressed solvent than τ_c increases, but for the higher temperatures, T_1(SR) appears to dominant at low densities.

In summary, at low temperatures for both benzene and perfluorobenzene, the spin−lattice relaxation mechanism appears dominated by dipole/dipole interactions. Perfluorobenzene has a larger moment of inertia and larger spin−rotation coupling constants than benzene which become important at low densities/high temperatures where the spin−rotation relaxation mechanism dominates. One might anticipate that based solely on a free-rotor argument (see eq 6) at constant density, T_1(DD-intra) for benzene should be larger than perfluorobenzene due to its smaller moment of inertia. In a comparable manner at constant density, T_1(DD-inter) for benzene should be larger than perfluorobenzene due to benzene's larger diffusion coefficient under similar experimental conditions, while for most of the experimental data, the T_1 value for benzene is larger than the T_1 value for perfluorobenzene at constant density (see Figure 4). This is not the case at the lower temperature/high density, where the T_1 values for the two compounds in CO_2 are similar.

If the relaxation mechanism is a thermally activated process than the activation energy can be expressed as

$$T_1 = T_1' \exp(-E_a/RT) \tag{9}$$

where E_a is the activation energy and R is the gas constant. Plotting ln T_1 against reciprocal temperature as in Figure 7, one can determine the activation energy from the slope. The values for benzene in CO_2 at ∼1100 atm and ∼2100 atm are 0.90 and 0.89 kcal/mol, respectively. The activation energy determined for pure liquid benzene in the two-phase region was 2.48 kcal/mol.[8] The activation energy for C_6F_6 was not determined due to its nonlinear behavior with temperature, except for the few values at low temperatures. The effect of the spin−rotation relaxation mechanism on T_1 can be seen in Figure 7. At ∼1100 atm, the T_1 values for C_6F_6 are collinear with benzene at low temperatures/high density. As temperature increases and density decreases the spin−rotation mechanism dominates the relaxation process and decreases T_1 as compared to benzene. The same behavior is seen at ∼2100 atm, except the collinear region for C_6F_6 extends to high temperatures. This is due to the higher initial density at this pressure, where the spin−rotation relaxation mechanism becomes dominant at densities $\leq\sim$1.1 g/cm^3. This is similar to the T_1 data shown for the pure compounds in Figure 5, where at low temperatures/high densities of the liquid in the two-phase region the T_1 values become comparable.[7,8]

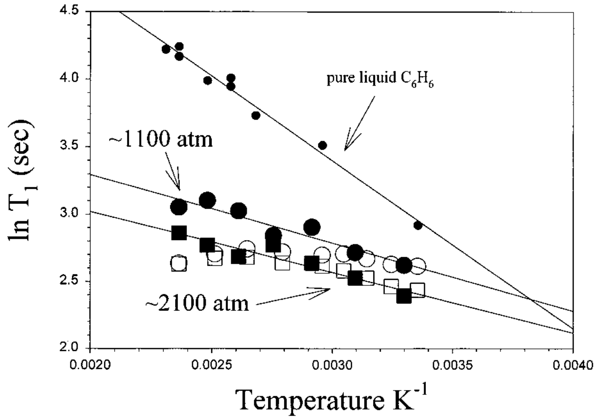

Figure 7. Plot of ln T_1 for benzene at ~1100 atm (●) and ~2100 atm (■) and for perfluorobenzene at ~1100 atm (○) and ~2100 atm (□) versus temperature in CO_2. Included for comparison is ln T_1 for pure liquid benzene (●) in the two-phase region over a similar temperature range.[8]

Conclusions

The measurement of the T_1 values for benzene, perfluorobenzene, and perdeuteriobenzene under similar experimental conditions of temperature and pressure in CO_2 solutions has been used to gain insight into the molecular level interaction of CO_2 with these compounds. Of particular interest was the determination if any specific molecular interactions between CO_2/F could be identified from the study of the solution dynamics of these solute molecules in CO_2 using high-pressure NMR. It was hypothesized that at high pressure/high density the specific interaction postulated to occur between CO_2 and fluorine should be more prevalent and this interaction could alter the relaxation rate/process of perfluorobenzene in solution as compared to benzene.

It is interesting to note the relative lack of a density dependence on the relaxation time for C_6F_6 as shown in Figures 3 and 4. At density values ≥0.8 g/cm^3 the relaxation times were very similar for the different temperatures investigated. Benzene had a greater variation with temperature and density. Comparing Figures 1−5, one can see that CO_2 has a large effect on the T_1 value of benzene in solution. The relative decrease in T_1 for benzene in CO_2 as compared to pure liquid benzene in the two-phase region is quite dramatic. There is a similar decrease in the T_1 value of C_6F_6 in CO_2, but it is not as large as that seen for benzene. The T_1 values for the solutes in CO_2 approach those of the pure liquids in the two-phase region at low temperatures. The decrease in T_1 between the CO_2/C_6H_6 solution and pure liquid benzene (two-phase region) is most likely due to quadrupole/quadrupole interactions between the CO_2 molecule and the benzene molecule in solution. All three of these molecules (CO_2, C_6H_6, and C_6F_6) have electric quadrupole moments,[17] and quadrupole/quadrupole interactions should be prevalent in solution. It appears that the solvation interactions between benzene and CO_2 are effective at reestablishing the Boltzmann equilibria of the nuclei after excitation in the fluid phase, which leads to the net reduction in T_1 times.

The effect of density is shown in Figure 6, where at high densities/low temperatures the relaxation times for both C_6F_6 and C_6H_6 are similar. The relaxation time for C_6D_6 is shorter than for the other two solute molecules due to quadrupolar relaxation, which is the interaction between the nuclear quadrupole moment and the fluctuating electric field gradient at the nucleus. Using C_6D_6 allows one to separate the intermolecular from the intramolecular dipole/dipole relaxation contributions for this series of solute molecules as the molecular reorientation correlation time in eq 5 is the same as the molecular reorientation correlation time in eq 2. For benzene the dipole/dipole intramolecular relaxation time calculated from eq 2, which is a function of the time dependence of the angle coordinates of the vector connecting the spin $^1/_2$ nuclei on the same molecule, is dominant throughout most of the density range. At higher densities for benzene, the dipole/dipole intermolecular relaxation mechanism (relaxation time calculated from eq 4), in which the vector connecting the two spin $^1/_2$ nuclei on different molecules in solution is time dependent, begins to play a more dominant role in molecular relaxation as the diffusion coefficient changes. This is similar to the T_1 results reported for methanol as a function of pressure and temperature.[11] For C_6F_6 the relaxation mechanisms are similar at low temperatures as compared to benzene. At high temperatures, the spin−rotation relaxation mechanism (relaxation time calculated from eq 5), which is caused when the molecule rotates as the rotation of charge creates a magnetic field at a point within the molecule, effects nuclear relaxation. This relaxation process is dependent on the change in the angular velocity of the molecule, which can be related to the number of molecular collisions a molecule undergoes. At high temperature/low density spin−rotation becomes a major factor in molecular relaxation as reported for benzene near its critical temperature[7,8] and methanol.[11] The difference between the T_1 value for benzene and the marked decrease in T_1 for ^{19}F at 423 K with decreasing density is due to spin−rotation relaxation. ^{19}F is affected to a much greater degree than ^1H since C_6F_6 has a larger moment of inertia than benzene ($I_{C_6F_6}/I_{C_6H_6} = 5.6$) and the spin−rotation coupling constants are larger for ^{19}F than ^1H and appear squared in eq 4.

In Figure 7, the Arrhenius plot of T_1 for the thermally activated relaxation process at two pressures shows the nonlinear behavior of C_6F_6 as a function of temperature. This is a result of the dual relaxation mechanism prominent for C_6F_6, where not only intramolecular dipole/dipole interactions play a role but spin−rotation interactions become significant at high temperatures and low density. There appears to be a specific density value (or narrow density range) over which the transition from dipole/dipole relaxation to spin−rotation relaxation occurs. This density value for both pressures shown in Figure 7 is ~1.1 g/cm^3. One would anticipate that the change in relaxation mechanism would be most prevalent for solutions at lower pressures where temperature can change density over a wider range. This is the case for ~1100 atm where the deviation from the CO_2/benzene data is readily apparent at lower temperatures than that seen at ~2100 atm. In both pressure cases, benzene demonstrates linear behavior in the Arrhenius plot, which confirms that a single relaxation mechanism is in operation for this solution. Since at low temperature for both pressures the T_1 values for the two different solutions merge, one could extrapolate that the same relaxation mechanism is prevalent for both molecules under these experimental conditions. The activation energy for molecular relaxation in the CO_2/benzene solution is much smaller than that determined for pure benzene. The activation energy for benzene (solid) is 4.1 kcal/mol,[14] while that determined for liquid benzene (two-phase region) over a temperature range of 303−423 K was 2.5 kcal/mol,[8] and the activation energy for the CO_2/benzene solution is 0.90 kcal/mol, which represents a low barrier to rotation of benzene in CO_2.

As apparent in these measurements of the relaxation times for C_6F_6 and C_6H_6 in CO_2 over similar pressures and temperatures, there is no experimental manifestation of a specific intermolecular interaction between CO_2 and fluorine. These interactions, if prevalent, would be expected to be seen in a change in relaxation rate or mechanism at high densities where the intermolecular distance between the CO_2 molecule and the fluorine group would be the smallest and their potential specific interaction the greatest. It appears at these high densities, solution viscosity dominates the relaxation process and the relaxation time for both ^{19}F and ^{1}H are the same. Thus, this experimental effort supports the calculations of Diep et al.[5] and the experimental efforts of Yee et al.[2] Overall, this effort helps confirm the lack of a specific CO_2/fluorine interaction for sub- and supercritical CO_2 solutions, it still remains to be determined what is the mechanism of enhanced solubility of fluorinated compounds in CO_2.

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