The Structure of Carbon Dioxide around Naphthalene Investigated using H/D Substitution in Neutron Diffraction

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The technique of hydrogen/deuterium substitution in neutron diffraction has been used to investigate the intermolecular structure of carbon dioxide saturated with naphthalene at supercritical pressure. The experiment was performed at $P = 206$ bar and $T = 302$ K, corresponding to a dilute concentration of approximately 1 $C_{10}H_8$ molecule to 110 CO_2 molecules. Particular attention has been paid to the local structural environment of the hydrogen atoms through the extraction of the first-order neutron difference function. The neutron data show that eight nearest-neighbor CO_2 molecules form a well-defined ring around the hydrogen atoms on the naphthalene molecule. Moreover, the CO_2 molecules appear to be oriented perpendicular to the plane of the naphthalene molecule at a distance of $r_{H-CO2} = 3.3$ Å.

Introduction

The solubility of solids in near-supercritical fluids can vary strongly with respect to changes in temperature and pressure. In many cases, the local microstructure of the supercritical fluid around the solute is known to be appreciably different from that of the bulk solvent.[1,2] The current understanding of solvation in dilute mixtures suggests that the solvent molecules form a cage around the solute. Because of the short-range nature of the lowest-order quadropole−quadropole and van der Waals interactions that dominate in typical solvents such as carbon dioxide ($T_c = 304.1$ K, $P_c = 73.8$ bar), understanding these short-range variations in microstructure is important[3]. However, because the high compressibility of the near-critical solvent allows large clusters to form, many recent experiments have concentrated on long-range structure around the solute molecule.[4] Recent RISM integral equation theory calculations of the radial distribution function[5] and molecular mechanics simulations[6] have predicted the preferred orientations of the first shell of carbon dioxide molecules around a naphthalene molecule (see Figure 1). Naphthalene dissolved in carbon dioxide has become a model system for studying these solubility effects.[5−7] As both of these molecules can be regarded as rigid and symmetric, they are good candidates for structural investigations of the solvent−solute interaction by experimental, theoretical, and simulation techniques. The primary objective of this work is to investigate the short-range structural correlations of the CO_2 molecules around the naphthalene molecule. To achieve this end, we have applied the powerful technique of hydrogen/deuterium (H/D) substitution in neutron diffraction[8] to probe the local structural environment of the solvated naphthalene molecule in carbon dioxide at supercritical pressure and near-critical temperature.
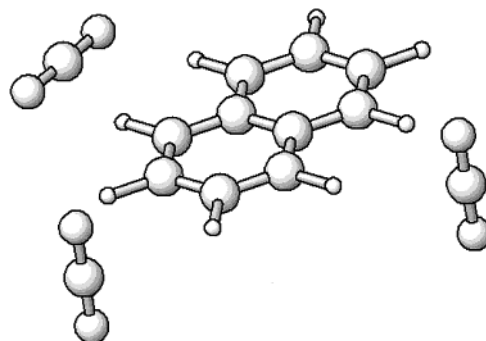
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Figure 1. Three most favorable configurations for a carbon dioxide molecule around the aromatic rings of a naphthalene molecule as predicted by a recent RISM calculation.[5] Labeled from the top left CO_2 molecule in an anticlockwise direction: (a) the "parallel" configuration, (b) the "T-shaped" configuration, and (c) the "twisted" configuration.

Experiment

Experiments were performed on the SANDALS neutron diffractometer at the ISIS spallation source in the U.K. Two separate measurements were carried out on fully protonated and fully deuterated naphthalene powder dissolved in carbon dioxide. In each case, a mass of 137 ± 1 mg of naphthalene powder was placed in the bottom of a titanium−zirconium container, just below the level of the neutron beam, and heated to 302 K (a few degrees below T_c for pure CO_2). Carbon dioxide gas was then introduced into the container, and the pressure increased slowly to 206 ± 3 bar. The carbon dioxide fluid saturated with naphthalene (now in the path of the neutron beam) was allowed to equilibrate for 1 h, and once stable, diffraction patterns were measured for both $C_{10}H_8$ and $C_{10}D_8$ dissolved in CO_2 at supercritical pressure. Although the precise temperature of the sample was not accurately measured, both experiments were performed under identical and stable conditions to within a temperature variation of 0.1 K of each other. A measure of the solubility of the naphthalene in carbon dioxide, accurate to within about $\pm 5\%$, was obtained from the neutron measurement. For the conditions described, the solubility was found to be approximately 0.009 mole fraction, which is in agreement with litera-

ture values.[9,10] Additional measurements performed at $T = 322$ K and $P = 206$ bar indicated some crystallization of the naphthalene on the container walls and so are not presented here.

Theoretical Comments and Data Analysis

The data were analyzed using the ATLAS package,[11] which corrects for container scattering, attenuation, multiple scattering, and nuclear recoil. The results in this paper follow the usual convention and are presented as neutron structure factors, $S(Q)$.

For a multicomponent system, the measured neutron interference function $F(Q)$ and total structure factor $S(Q)$ are given by a linear combination of neutron-weighted Faber–Ziman partial structure factors, $S_{\alpha\beta}(Q)$.

$$F(Q) = \sum_\alpha \sum_\beta c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta [S_{\alpha\beta}(Q) - 1] \quad (1)$$

where c_α is the atomic fraction and $\bar{b}_\alpha$ the neutron scattering length of chemical species α. It follows that, for pure CO_2, we have contributions from three weighted partial structure factors.[8,11]

$$S_{CO2}(Q) = 0.132[S_{CC}(Q) - 1] + 0.406[S_{OO}(Q) - 1] + 0.462[S_{CO}(Q) - 1] \quad (2)$$

As H and D have different neutron scattering lengths, by performing identical experiments on fully protonated and fully deuterated naphthalene dissolved in CO_2, the neutron weighting factors involving the hydrogen interactions alone can be extracted through a first-order difference method.[8,12]

$$S_{XH}(Q) = \frac{F_{C10D+CO2}(Q) - F_{C10H8+CO2}(Q)}{\displaystyle\sum_H \sum_\alpha c_H c_\alpha \bar{b}_H \bar{b}_\alpha} \quad (3)$$

The remaining interactions (plus a small additional HH contribution[13]), which in this case are dominated by the CO_2 molecules, can also be extracted through the equation

$$S_{XX}(Q) = \frac{F_{C10H8+CO2}(Q) - AF_{XH}(Q)}{\displaystyle\sum_\alpha \sum_\beta c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta} \quad (4)$$

where $A = [b_D/(b_D - b_H)] = 0.641$. The measured structure factors for these three functions are shown in Figures 2 and 3. The measured structure factor, $S(Q)$, is directly related to the radial distribution function, $G(r)$, through Fourier transformation[8] (using number densities of 0.031 atoms Å^{-3} for pure CO_2[14] and 0.039 atoms Å^{-3} for the mixture[15]). To Fourier transform the Q-space curves shown in Figures 2 and 3, a maximum entropy routine[8] was employed to reduce spurious artifacts. The normalized neutron weighting factors for the above naphthalene concentration are as follows:

$$G_{XH}(r) = G_{XH}{}^{intra}(r) + G_{XH}{}^{inter}(r)$$
$$= 0.612 g_{HO}{}^{inter}(r) + 0.350 g_{HCo}{}^{inter}(r) + 0.032 g_{HCn}(r) + 0.006 g_{HH}(r) \quad (5)$$

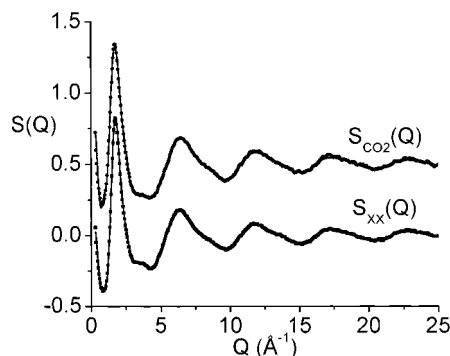**Figure 2.** Measured neutron structure factors for (i) $S_{CO2}(Q)$, supercritical CO_2 at $T = 322$ K and $P = 206$ bar; and (ii) the S_{XX}-(Q) function for 0.009 mole fraction naphthalene dissolved in carbon dioxide at $T = 302$ K and $P = 206$ bar. The symbols represent the measured data, and the solid line is a maximum entropy fit to the data. The top curve is shifted by 0.5 for clarity.
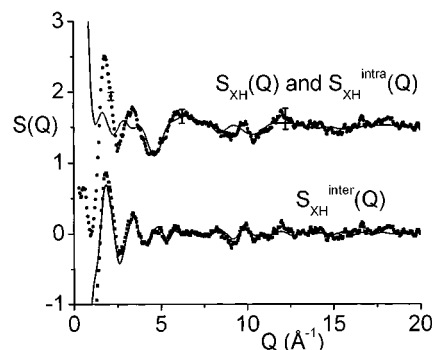

Figure 3. Measured first-order difference function, $S_{XH}(Q)$ (top, circles), for 0.009 mole fraction $C_{10}D_8$ in CO_2 (at $T = 302$ K, $P = 206$ bar, $\rho = 0.039$ atoms Å^{-3}, shifted by 1.5), with some typical error bars. The solid line (top) corresponds to $S_{XH}{}^{intra}(Q)$, the calculated contribution from intramolecular naphthalene interactions alone. The squares (lower curve) correspond to the difference $S_{XH}{}^{inter}(Q) = S_{XH}(Q) - S_{XH}{}^{intra}(Q)$ and represent the intermolecular interactions of the hydrogen atoms on the naphthalene molecule. The solid line is a maximum entropy fit to $S_{XH}{}^{inter}(Q)$ with the constraint that $G_{XH}{}^{inter}(r) = 0$ for $r < 3.0$ Å.

$$G_{XX}(r) = 0.434 g_{CoO}(r) + 0.379 g_{OO}(r) + 0.124 g_{CoCo}(r) + 0.039 g_{CnO}{}^{inter}(r) + 0.023 g_{CoC}{}^{inter}(r) + 0.001 g_{CnCn}(r) + 0.0004 g_{HH}(r) \quad (6)$$

where Cn represents the carbon atoms from the naphthalene and Co the carbon dioxide. It is important to note that the measured difference functions $G_{XH}(r)$ and $G_{XX}(r)$ have neutron-weighted contributions from both intra- and intermolecular partial correlation functions unless otherwise specified.

In the first-order difference function shown in Figure 3, we have separated out the intra- and intermolecular hydrogen interactions from our measured data. The intramolecular hydrogen naphthalene–naphthalene contributions $S_{HCn}{}^{intra}(Q)$ and $S_{HH}{}^{intra}(Q)$ were calculated for a rigid naphthalene molecule in the fluid by fitting to the neutron spectra using the molecular structure function $S_m{}^{intra}(Q)$

$$S_m{}^{intra}(Q) = \frac{\displaystyle\sum_\alpha \sum_\beta \bar{b}_\alpha \bar{b}_\beta \frac{\sin(Qr)}{r} \exp\left(\frac{-Q^2\sigma^2}{2}\right)}{\displaystyle\sum_\alpha \sum_\beta \bar{b}_\alpha \bar{b}_\beta} \quad (7)$$
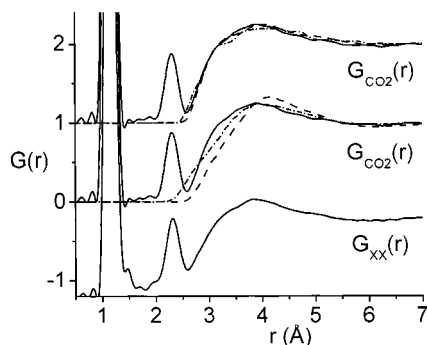
Figure 4. The solid lines in the top (shifted by +1.0) and middle curves represent the real space functions corresponding to pure supercritical carbon dioxide, $G_{CO2}(r)$ at $T = 322$ K, $P = 206$ bar, $\rho = 0.031$ atoms Å^{-3}. The bottom solid line represents the $G_{XX}(r)$ function for 0.009 mole fraction $C_{10}D_8$ in CO_2 (at $T = 302$ K, $P = 206$ bar, $\rho = 0.039$ atoms Å^{-3}, shifted by −1.2). These curves correspond to the Fourier transforms of the $S_{CO2}(Q)$ and $S_{XX}(Q)$ solid curves shown in Figure 2. The dashed and dash−dotted lines of the top data set represent the molecular dynamics simulations and published neutron data on pure supercritical CO_2 by Ishii et al.,[18] taken at $T = 310$ K, $P = 101$ bar, and $\rho = 0.029$ atoms Å^{-3}. The dashed and dash−dotted lines of the middle data set represent the intermolecular structure of CO_2 obtained from RISM calculations and Monte Carlo simulations[5] for pure CO_2 at $T = 400$ K and $\rho = 0.029$ atoms Å^{-3}.

where $\sigma_{\alpha\beta}$ represents the root-mean-square displacement of the mean interatomic distance $r_{\alpha\beta}$. The best intramolecular naphthalene fit was obtained using bond lengths of $r_{CnH} = 1.13(1)$ Å and $r_{CnCn} = 1.43(1)$ Å, with root-mean-square displacements of $\sigma_{CnH} = 0.078$ Å (for a bonded interaction), $\sigma_{CnH} = 0.12$ Å (nonbonded), and $\sigma_{HH} = 0.12$ Å. By (in effect) normalizing the area of the real-space neutron difference spectra to the intramolecular structure of the naphthalene molecule, it was possible to obtain a reasonable measurement of the naphthalene solubility,[16] which was found to be 0.009 ± 0.0005 mole fraction. Consequently, the difference, $G_{XH}^{inter}(r) = G_{XH}(r) - G_{XH}^{intra}(r)$, shown in Figure 4, yields primarily intermolecular naphthalene hydrogen−CO_2 interactions, as well as a small contribution from intermolecular naphthalene hydrogen−naphthalene interactions (see eq 5).

Results and Discussion

The measured radial distribution functions for pressurized carbon dioxide and supercritical carbon dioxide with 0.009 mole fraction naphthalene are shown in Figures 4 and 5. The CO_2 spectra can be split into two parts: the dominant C−O and O−O intramolecular peaks at $r_{CO} = 1.16(1)$ Å and $r_{OO} = 2.32(1)$ Å and the broader intermolecular contributions at higher r (>2.5 Å). Supercritical fluid CO_2 has been widely studied using neutron scattering techniques,[17,18] showing that the structure primarily depends on density rather than temperature. Using this as a justification, we compare our supercritical CO_2 data with published neutron data, molecular dynamics simulations, RISM calculations, and Monte Carlo simulations[5] performed at pressures and temperatures different from those used in our experiments, but at a very similar density. The main features of the measured intermolecular CO_2 structure compared to published neutron[18] and molecular dynamics simulation curves are in good agreement, whereas the RISM and Monte Carlo simulations are in approximate agreement (see Figure 4).
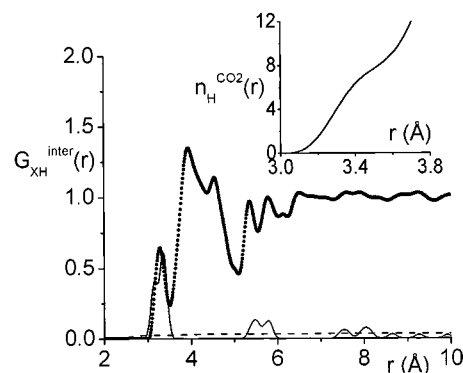

Figure 5. First-order difference function $G_{XH}^{inter}(r)$ in real space (circles), showing the environment of the hydrogen atoms on the naphthalene molecule [per atom, obtained by Fourier transform of the solid curve of $S_{XH}^{inter}(Q)$ in Figure 3]. The solid line corresponds to contributions from the distinct CO_2 in-plane ring structure illustrated in Figure 6. The dashed line corresponds to naphthalene−naphthalene correlations for pure liquid naphthalene[20] scaled by the neutron weighting factor for this experiment (see text). Inset: Running coordination number $n_H CO2(r)$ (shown per molecule), obtained from the first-order difference function, $G_{XH}^{inter}(r)$. The curve was calculated assuming hydrogen−CO_2 correlations only and represents a tally of the number of CO_2 molecules surrounding a central hydrogen molecule at a particular distance.

The first-order difference curve in Figure 5, showing the environment of the naphthalene hydrogen atoms, reveals three main regions: (i) a well-defined nearest-neighbor peak at 3.3 Å, (ii) followed by pronounced region out to 5.0 Å with peaks at 3.9 Å and 4.6 Å, and (iii) a series of high-r correlations extending out to at least 10 Å. Although relatively short-range intermolecular hydrogen naphthalene−naphthalene contributions may occur,[19,20] the neutron weighting factors (given in eq 5) on the $g_{HCn}(r)$ and $g_{HH}(r)$ partial distribution functions make their contribution to $G_{XH}^{inter}(r)$ very small compared to the $g_{H-CO2}(r)$ contributions. To illustrate this point, we have taken the neutron-weighted sum (for this experiment) of the intermolecular $g_{DCn}^{inter}(r)$ and $g_{DD}^{inter}(r)$ partial distribution functions estimated from neutron scattering results on pure deuterated liquid naphthalene[21] and shown this curve in Figure 5. From the magnitude and broad featureless shape of this curve, it follows that the structural peaks in the measured $G_{XH}^{inter}(r)$ function are probably almost entirely CO_2−naphthalene contributions. Integrating under the first nearest-neighbor peak, assuming only H−CO_2 interactions, yields an average of eight CO_2 molecules around a naphthalene molecule, as shown by the running coordination number, $n_H^{CO_2}(r)$ (per molecule); see inset in Figure 5. Various different orientations of the CO_2 molecules around the hydrogen atoms were attempted to fit the exact shape of the nearest-neighbor peaks in the neutron data. The only CO_2 orientations found to give reasonable fits were the "twisted" and "T-shaped" configurations predicted by the RISM calculations shown in Figure 1. Moreover, the neutron data suggest that all eight CO_2 nearest-neighbor molecules are oriented perpendicular to the plane of the naphthalene molecule to form a ringlike solvation shell. An illustrated example of the structure is given in Figure 6. Because of the limited resolution of the measurement, the neutron H−C_O and H−O peaks appear to overlap at around 3.3 Å, whereas in the model shown (which does not contain resolution effects), the
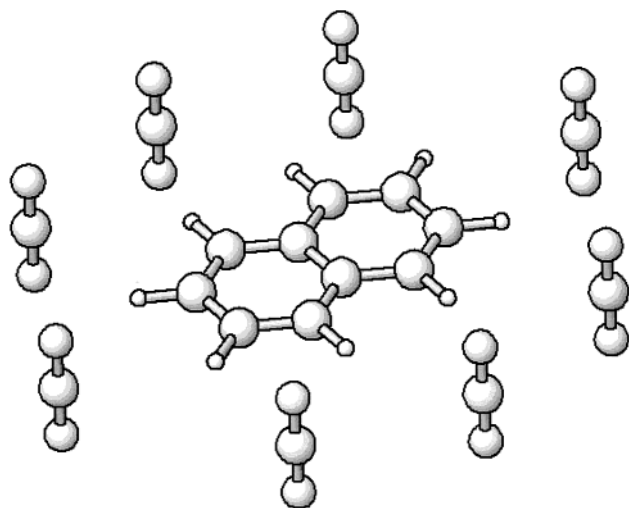
Figure 6. Preferred orientation of the nearest-neighbor CO_2 molecules around the hydrogen atoms on the naphthalene molecule consistent with the neutron data.

two peaks are present at $r_{HC} = 3.16$ Å and $r_{HO} = 3.37$ Å, both with fitted rms displacements of $\sigma_{HX} = 0.08$ Å.

A similar ring structure of eight in-plane nearest-neighbor CO_2 molecules around a naphthalene molecule has also been predicted by molecular mechanics simulations.[6] During the simulated supercritical fluid extraction run, those authors[6] found that, as additional CO_2 molecules are added, the first eight nearest-neighbor molecules surround the center of the naphthalene ring structure, as observed in the neutron data. However, if more CO_2 molecules are added after this shell is filled, the simulation predicts that the solvent cage becomes completely randomized. In addition, Raman[22] studies also predict an out-of-plane face-to-face charge-transfer complex between the CO_2 and the center of the naphthalene at a distance of 3.5 Å. Although the neutron data clearly show hydrogen correlation distances in this region, the specific orientation of the CO_2 interactions beyond the nearest-neighbor distance are not yet clear.

Conclusions

The technique of H/D substitution in neutron diffraction has been applied to naphthalene dissolved in carbon dioxide at $T = 302$ K, $P = 206$ bar (0.009 mole fraction naphthalene). The isotopic difference results show a distinct ring of eight CO_2 molecules surrounding the naphthalene molecule at a distance of 3.3 Å, which appear to be oriented perpendicular to the plane of the naphthalene molecule. These results agree qualitatively with recent RISM calculations and molecular mechanics simulation studies already in the literature.[5,6] Structural peaks due to specific orientational correlations of molecules around the solute naphthalene are also observed at distances of 3.9 and 4.6 Å away from the hydrogen atoms.

A more comprehensive series of isotopic substitution neutron diffraction experiments on the CO_2–naphthalene system are planned to investigate the structural changes over a range of temperatures and pressures. Interpretation will be aided by molecular dynamics simulations to help elucidate the likely structures associated with the well-defined ordering observed at larger distances in the CO_2 solvation shell.

Literature Cited

(1) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. Supercritical Fluids as Solvents for Chemical and Materials Processing. *Nature* **1996**, *383*, 313–318.

(2) Otomo, J.; Koda, S. UV Absorption Shifts of Benzenes in Supercritical Carbon Dioxide. *Chem. Phys.* **1999**, *242*, 241–252.

(3) Chialvo, A. A.; Cummings, P. T. Molecular Based Modelling of Water and Aqueous Solutions at Supercritical Conditions. *Adv. Chem. Phys.* **1999**, *109*, 115.

(4) Eastoe, J.; Cazelles, B. M. H.; Steytler, D. C.; Holmes, J. D.; Pitt, A. R.; Wear, T. J.; Heenan, R. K. Water-in-CO_2 Microemulsions Studied by Small-Angle Neutron Scattering. *Langmuir* **1997**, *13*, 6980–6984.

(5) Koga, K.; Tanaka, H.; Zeng, X. C. RISM Integral Equation Study of Local Solvation Behaviour of Naphthalene in Supercritical Carbon Dioxide. *J. Phys. Chem.* **1996**, *100*, 16711–16719.

(6) Battersby, P.; Dean, J. R.; Hitchen, S. M.; Tomlinson, W. R.; Myers, P. M. Interaction between Carbon Dioxide and Naphthalene: A Molecular Modeling Approach. *J. Comput. Chem.* **1994**, *15*, 580–587.

(7) Joslin, C. G.; Gray, C. G.; Goldman, S.; Tomberli, B.; Li, W. Solubilities in Supercritical Fluids from the Virial Equation of State. *Mol. Phys.* **1996**, *89*, 489–503.

(8) Soper, A. K.; Luzar, A. Combined Neutron Diffraction and Computer Simulation Study of Liquid Dimethyl Sulphoxide. *J. Chem. Phys.* **1993**, *99*, 6836–6847.

(9) Mitra, S.; Chen, J. W.; Viswanath, D. S. Solubility and Partial Molar Volumes of Heavy Aromatic Hydrocarbons in Supercritical CO_2. *J. Chem. Eng. Data* **1988**, *33*, 35–37.

(10) McHugh, M.; Paulaitis, M. E. Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1980**, *25*, 326–329.

(11) Soper, A. K.; Howells, W. S.; Hannon, A. C. *ATLAS– Analysis of Time-of-Flight Diffraction Data from Liquid and Amorphous Samples*; Technical Report RAL 89-046; Rutherford Appleton Laboratory: Chilton, Oxon, U.K., 1989.

(12) Powles, J. G. The structure of molecular liquids by neutron scattering. *Adv. Phys.* **1973**, *22*, 1–56.

(13) The way the XX function has been defined in this analysis, a weighted HH partial contribution appears in both the XH and XX functions; see eqs 2–4 in ref 8.

(14) Ely, J. F.; Haines, W. M.; Bain, B. C. Isochoric (P, V_m, T) measurements on CO_2 and on ($0.982CO_2 + 0.018N_2$) from 250 to 330 K at pressures to 35 MPa. *J. Chem. Thermodyn.* **1989**, *21*, 879.

(15) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Kim, S. Solute Partial Molar Volumes in Supercritical Fluids. *J. Chem. Phys.* **1986**, *90*, 2738–2746.

(16) The solubility was determined by an iterative process. The total neutron structure factors were analysed at different CO_2–naphthalene concentrations until the area obtained under the well-defined peak in $G_{XH}^{intra}(r)$ at 1.13 Å was consistent with the known coordination of the intramolecular naphthalene C–H bond.

(17) Chiappini, S.; Nardone, M.; Ricci, F. P. Neutron Diffraction Measurements on High-Pressure Supercritical CO_2. *Mol. Phys.* **1996**, *89*, 975–987.

(18) Ishii, R.; Okazaki, S.; Okada, I.; Furusaka, M.; Watanabe, N.; Misawa, M.; Fukunaga, T. Density Dependence of Structure of Supercritical Carbon Dioxide Along an Isotherm. *J. Chem. Phys.* **1996**, *105*, 7011–7021.

(19) Cochran, H. D.; Pfund, D. M.; Lee, L. L. Study of Flucuations in Supercritical Solutions by an Integral Equation Methodology. *Proc. Int. Symp. Supercritical Fluids* **1988**, 245–252.

(20) Wu, R.-S.; Lee, L. L.; Cochran, H. D. Structure of Dilute Supercritical Solutions: Clustering of Solvent and Solute Molecules and the Thermodynamic Effects. *Ind. Eng. Chem. Res.* **1990**, *29*, 977−988.

(21) Misawa, M.; Fukunaga, T. Structure of Liquid Benzene and Naphthalene Studied by Pulsed Neutron Total Scattering. *J. Chem. Phys.* **1990**, *93*, 3495−3502.

(22) Zerda, T. W.; Song, X.; Jonas, J. Raman Study of Intermolecular Interactions in Supercritical Solutions of Naphthalene. *Appl. Spectrosc.* **1986**, *40*, 1194−1199.