Conformation Equilibrium of 1,2-Dichloroethane as a Probe for Solvent Properties of Liquid and Supercritical CO_2

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Gibbs-energy difference between the gauche and trans isomers of 1,2-dichloroethane (DCE) in liquid and supercritical (SC) CO_2 was investigated using Raman spectroscopy. The gauche isomer was relatively stabilized in these solvents compared with in non-polar organic solvents. This was attributed to the interaction of the dipolar gauche isomer with the quadrupole moment of the CO_2 molecule, as well as the local density enhancement in SC CO_2. Conformation equilibrium of DCE was suggested to be useful as a probe for studying solvent properties of SC fluids.

SC fluids are used as solvents for chemical and material processing in industrial plants, as well as in research laboratories.[1] Among the compounds used as SC fluids, CO_2 is especially useful in many respects.[2] Thus, CO_2 is the most popular compound used as a SC fluid.

It should be noted that the CO_2 molecule has no molecular dipole moment and a small polarizability. Thus, SC CO_2 is sometimes recommended only for the treatment of non-polar substances.[2] However, as a matter of fact, SC CO_2 has been used for the treatment of rather polar substances such as food ingredients.[1] What is the source of these unique properties of SC CO_2? It has been inferred that the quadrupole moment of CO_2 molecules stabilizes polar solute molecules,[3,4] and also that site-specific solute-solvent interactions including hydrogen bonds might be the source of the versatility of SC CO_2.[4] For the assessment of the properties of CO_2 as a solvent, it is important to know thermodynamic behavior of the solute. For this purpose, we studied the conformation equilibrium of DCE in liquid and SC CO_2 by Raman spectroscopy.

DCE is a well-known compound for which the existence of conformation isomers was studied by Raman spectroscopy in early days of structural chemistry.[5] Herein, we report novel findings in which the Gibbs-energy difference ΔG between the polar gauche and non-polar trans isomers of DCE is smaller in liquid or SC CO_2 than that in ordinary solvents of comparable dielectric constants. This behavior of DCE is useful for examining the solvent properties of SC fluids.

The instrument and method used to acquire the Raman measurements on SC binary fluids were the same as those reported previously.[6] The details of spectral analyses will be described elsewhere.[7] The sample composition in the cell was determined by comparing the intensity ratio between the Raman bands of DCE and CO_2 with the data obtained for samples of known compositions. The mole fraction of DCE was about 0.001 throughout this work to diminish the interaction between the DCE molecules.

An example of the wide-range spectrum of a DCE solution in SC CO_2 is shown in Figure 1. The very weak bands around 660 and 760 cm^{-1} are the symmetric C–Cl stretching bands of the gauche and trans molecules of DCE, respectively, and the bands around 1280 and 1380 cm^{-1} attributed to CO_2 are the bands brought about by the Fermi resonance between the C=O stretching mode and the second harmonic of the O–C–O bending mode. The weak bands around the strong CO_2 bands are attributed to molecules with heavy isotopes.[8]

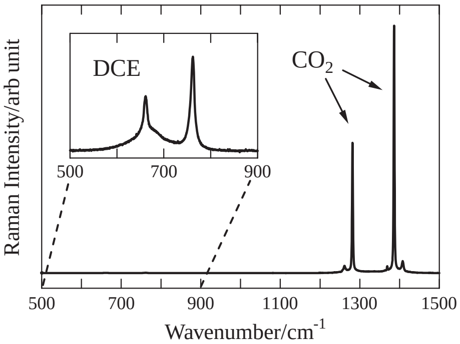

Figure 1. Raman spectra of a DCE solution in SC CO_2 at 307.3 K ($T/T_c = 1.01$) and 15.69 MPa. Mole fraction of DCE was 0.0012. The insert shows the DCE bands with the ordinate magnified by 500 times.

Figure 2 shows an example of the analysis of the gauche (A) and trans (B) symmetric C–Cl stretching bands of DCE. See the figure caption for the assignments of the underlying additional bands, C and D. We carefully examined the nature of C and D in the spectra measured at a wide range of pressure as well as in the polarized spectra obtained for DCE/CO_2 solutions and neat CO_2.[7] By fitting the spectra with four Lorentz functions, we estimated the ratio of the integrated intensities, I_g and I_t, of the bands, A and B.

For estimating the mole fraction of the gauche isomer from the Raman data, we measured the ratio of the Raman-scattering cross sections, σ_g and σ_t, of the A and B bands in Figure 2 on gaseous pure DCE with the aid of the thermodynamic data.[9] We found $\sigma_g/\sigma_t = 0.42$, which is close to the value 0.39 for liquid DCE.[9] Thus, we employed the value 0.42 throughout the present work. The mole fraction x_g of the gauche isomer within the solute DCE was estimated by the relation, $x_g = I_g\sigma_t/(I_g\sigma_t + I_t\sigma_g)$.

Figure 3 shows the density dependence of x_g in SC CO_2 at $T/T_c = 1.01$, where the abscissa indicates the density relative to the critical density ρ_c of CO_2. The pink diamond indicates x_g observed for gaseous DCE at 296 K, and the solid line indicates x_g calculated using the Onsager model.[10] The solid line shows the increase of x_g with the increase of density, indicating the stabilization of the gauche isomer due to the electrostatic interaction between its dipole moment and the solvent. It should be noted that the observed x_g is larger than expected by the Onsager model in a wide range of density. The local density enhancement

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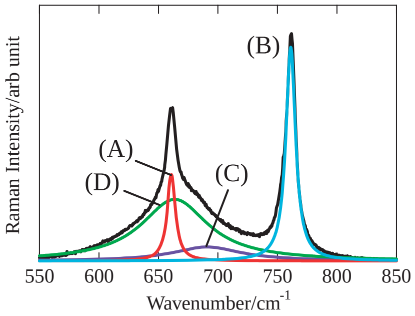

Figure 2. An example of the analysis of DCE Raman bands in SC CO_2. The sample was the same as that used in Figure 1. The following four components were assumed; (A) symmetric C–Cl stretching of gauche, (B) symmetric C–Cl stretching of trans, (C) antisymmetric C–Cl stretching of gauche, (D) Raman-forbidden bending of CO_2 induced by high pressure and by the interaction with DCE molecules.

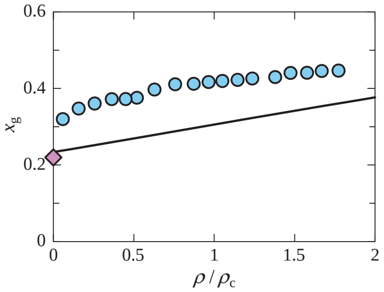

Figure 3. Blue circles: density dependence of the mole fraction x_g of gauche DCE in SC CO_2 at 307 K, where x_g stands for the fraction of gauche within the solute DCE. Pink diamond: x_g in gaseous DCE at 296 K. Solid line: x_g calculated using the Onsager model.

in SC CO_2 is thought to favor the electrostatic stabilization of the gauche isomer. However, this mechanism is considered to be effective only in the density region around ρ_c. The fact is that the observed x_g is fairly large compared with the value by the Onsager model in the smaller density region and also in the region around $2\rho_c$ where the density fluctuation is calmed.[11] These behaviors are different from those in other SC fluids,[7] and a relevant issue will be described below.

We calculated ΔG between the gauche and trans isomers in SC CO_2 using the relation,[9]

$$\Delta G = -RT\ln\{I_g\sigma_t/(2I_t\sigma_g)\},$$

and plotted it with blue circles in Figure 4 against the quantity $(\varepsilon - 1)/(2\varepsilon + 1)$ that is known as the Onsager function, where ε represents the dielectric constant of the solvent. The data plotted with squares are the room-temperature ΔG in ordinary solvents and in the compressed liquids of CO_2, C_2H_6, and CHF_3. Most of the squares are approximately located on a single curve, as has been described by Wiberg et al.[12] This suggests that the stabilization of the gauche isomer in most solvents is given by the interaction between its electric dipole and the solvent.

It is noticed in Figure 4, however, ΔG in liquid and SC CO_2 at different pressures (the same original data used in Figure 3) and in benzene significantly deviates from the solid curve that represents the properties of ordinary solvents. The deviation of SC CO_2 in the medium density region might be attributed to the local density enhancement of the solvent as has been mentioned in the description for Figure 3, but the deviation in the smaller and larger density regions cannot be attributed to it. To explain these deviations, we recall that CO_2 and benzene have quadrupole moments.[3] Figure 4 clearly indicates the stabilization of the gauche isomer of DCE in liquid and SC CO_2 as in benzene, suggesting the significant effect of the quadrupole moment when CO_2 is used as the solvent. Finally, as it has been revealed by the dielectric and thermodynamic considerations described in this letter, the conformation equilibrium of DCE is promising as a useful probe for solvent properties of different SC fluids.

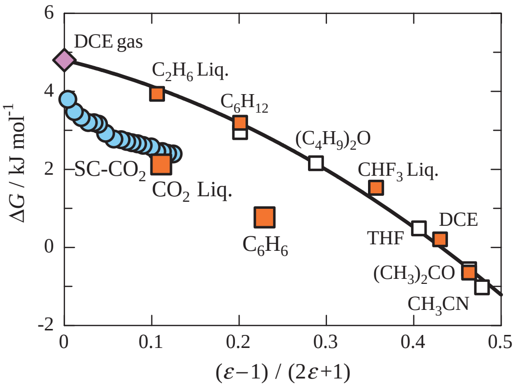

Figure 4. Gibbs-energy difference ΔG between the gauche and trans isomers of DCE in various solvents. The abscissa indicates the so-called Onsager function that is related to the dielectric constant ε of the solvent. Blue circles indicate ΔG in SC CO_2 of different pressures at 307 K. Other symbols indicate ΔG in other solvents at room temperature; pink diamond: in gaseous DCE, orange squares: in organic liquids and liquid CO_2 (present study), open squares: in organic liquids (Ref. 12).

References and Notes

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