

# STUDY OF TRANSPORT AND INTERMOLECULAR INTERACTIONS IN COMPRESSED SUPERCRITICAL FLUIDS

J. Jonas and D. M. Lamb

Department of Chemistry, School of Chemical Sciences  
University of Illinois, Urbana, Illinois 61801

General overview of several studies of transport and intermolecular interactions in compressed supercritical fluids will be presented. The unique aspects of the instrumentation used in these studies will also be emphasized. First, the results of NMR studies of self-diffusion in supercritical ethylene and toluene will be discussed. These experiments are using the fixed field gradient NMR spin-echo technique. Second, the novel NMR technique for the determination of solubility of solids in supercritical fluids will be described. Third, the promising potential of laser scattering experiments investigating interaction induced spectra will be illustrated on several specific studies of depolarized Rayleigh scattering. The interaction induced spectra offer valuable information about intermolecular interactions in supercritical fluids.

## Introduction

Research on the properties of supercritical fluids and supercritical fluid mixtures has become very important in recent years due to the great promise of supercritical fluid extraction techniques. These techniques and their applications have been reviewed by several authors (1-4). There are many advantages of using supercritical fluid extraction over conventional extraction techniques. Many low volatility molecular solids show greatly enhanced solubilities in supercritical dense fluids. Solvent recovery is easily accomplished by manipulating the density, and therefore the solvating power, of the supercritical fluid to precipitate the solid. In addition, although the densities of the supercritical fluids are comparable to liquid densities, the viscosities are generally an order of magnitude smaller, and diffusivities are an order of magnitude larger than liquids. A more efficient separation can therefore be achieved.

Unfortunately, there is a lack of fundamental data on transport and relaxation in model fluids at supercritical conditions. Not surprisingly, there is a corresponding lack of theoretical models to explain the dynamics of supercritical fluids on a molecular level, particularly at the intermediate densities.

The main purpose of our work is the improvement of molecular level understanding of solute-solvent interactions under supercritical conditions. Unique nuclear magnetic resonance (5) and laser scattering techniques (6) are employed to obtain new information about dynamics of molecules in supercritical fluids at high pressures.

The main results of several of our studies will be discussed. First, the results of NMR studies of self-diffusion in supercritical ethylene (7) and toluene (8) will be discussed. These experiments are using the fixed field gradient NMR spin-echo technique. Second, the novel NMR technique (9) for the determination of solubility of solids in supercritical fluids will be described. Third, the promising potential of laser scattering experiments investigating interaction induced spectra (6) will be illustrated on several specific studies of depolarized Rayleigh scattering.

## Experimental

The self-diffusion coefficients in supercritical ethylene were measured using the pulsed NMR spectrometer described elsewhere (10), automated for the measurement of diffusion coefficients by the Hahn spin echo method (11). The measurements were made at the proton resonance frequency of 60 MHz using a 14.2 kG electromagnet.

The pressure was generated using the gas compression system described previously (12). A Heise-Bourdon pressure gauge was installed between the compression system and the high pressure vessel to supplement the 30,000 psi pressure transducer. The oxygen scavenger system was bypassed as the amount of oxygen in the ethylene was below the minimum detection level (10 ppm) of the oxygen analyzer (Beckman Instruments, Inc.). In order to depress the extremely long  $T_1$  values of pure ethylene (13) at the experimental conditions studied, small quantities ( $< 1000$  ppm) of oxygen were mixed with the ethylene before measurement of the diffusion coefficient. The addition of oxygen brought the  $T_1$  values down to 2-3 sec, but should not affect the value of the diffusion coefficient. The shorter  $T_1$  values allowed a much shorter measurement time.

The self-diffusion coefficients in supercritical toluene- $d_6$  were measured at the deuterium resonance frequency of 9.21 MHz, using a 14.1 kG electromagnet with a wide gap (3.8") to accommodate the high pressure vessel. The pulsed NMR spectrometer and receiver system were described in detail elsewhere (10). The argon pressurized high pressure, high temperature NMR probe (14) was used previously for studies of relaxation (15) and diffusion (16) in compressed supercritical water. It consists of two high pressure vessels: the primary vessel, containing an internal furnace, two thermocouples and the RF coil and sample, and the secondary vessel, containing the stainless steel sample bellows. Quartz sample cells were used rather than ceramic cells, as corrosion is not a problem. The RF coil was constructed by winding 14 1/2 turns of 22 gauge nichrome (Chromel A) wire. The coil was silver soldered to nichrome conductor coaxial high pressure leads. The tuning circuit consisted of a six foot impedance transforming coaxial cable terminated with a tapped-parallel capacitor box with both fixed and variable capacitors totalling 70 pF in series and 10 pF in parallel. The observed signal peak to rms noise ratio in liquid toluene- $d_6$  (30°C) was 60:1 after one scan.

Some experimental detail (9) on the experimental NMR setup for the measurement of solubilities of organic solids in supercritical fluids will be given in the section dealing with Results and Discussion.

The description of equipment and experimental techniques for laser Rayleigh scattering experiments on supercritical fluids at high pressures were given earlier (6,17,18).

## Results and Discussion

### Self-Diffusion in Compressed Supercritical Ethylene

The main purpose of our work (7) was to provide transport data on dense supercritical ethylene and to analyze the data in terms of currently available theories. Ethylene was chosen for the study for a number of reasons. First, it is one of the most widely used solvents in industry due to its easily accessible critical temperature, its relatively low cost and wide availability. Highly accurate compressibility data are available (19,20,21) in the literature over a wide range of temperature and pressures. These data are necessary for a complete analysis of the transport data.

Some measurements have been made of self diffusion in pure ethylene and in ethylene-sulfur hexafluoride mixtures (22), but these measurements were made very close to the critical temperature and up to pressures of only about 100 bar. Proton spin-lattice relaxation times ( $T_1$ ) of ethylene have been measured at temperatures from 0°C to 50°C and pressures up to about 2300 bar (13). The relaxation time values were 40-50 sec for much of the region studied. Several relaxation mechanisms contribute to this long relaxation time and make both the measurement and analysis of the relaxation times very difficult. For these reasons, we decided to limit our study to the measurement of the self-diffusion coefficient in supercritical ethylene.

The measurements were made as a function of density for pressures from 1 - 2000 bar and at 50°, 75°, 100° and 125°C. The temperatures chosen correspond to those for which density data (19-21) for ethylene and ethylene-CO<sub>2</sub> are available.

The density dependence of the ethylene self-diffusion coefficients was analyzed using the Enskog theory (23) of diffusion of hard spheres corrected for the effects of correlated motion (24). The corrected Enskog theory considers only repulsive forces between molecules, but it has proved to be in excellent agreement with experiment for the transport coefficients of supercritical dense gases such as argon, krypton, methane and carbon tetrafluoride (25). At densities less than the critical density ( $\rho_c$ ), the attractive forces between the molecules become important and deviations from the theory are observed.

In previous work on supercritical fluids, Jonas et al. (26-28) measured self-diffusion, shear viscosity and angular momentum correlation times in very dense ( $\rho > 2\rho_c$ ) supercritical fluids of simple polyatomic molecules such as SF<sub>6</sub>, CF<sub>4</sub>, CFC1<sub>3</sub> and C<sub>4</sub>F<sub>8</sub>. The goal of the experiments was to investigate the applicability of the rough hard sphere (RHS) model (29) at very high densities. At these high densities, the harsh, short ranged repulsive forces screen out the long range attractive forces. The RHS model accounts for the coupling between rotational and translational motion and was found to agree well with the experimental data for  $\rho > 2\rho_c$ . However, at the lower densities, deviations between the theory and experiment were observed for angular momentum relaxation in CF<sub>4</sub> (12) and mixtures of CF<sub>4</sub> with argon and neon (30). These deviations were attributed to the effects of attractive forces, causing the RHS model to break down. A theoretical model based on optimized cluster theory (31) was proposed (12) to account for the effects of attractive forces and was found to give a good explanation of the experimental data.

Another problem with applying the Enskog theory to explain the ethylene data is that ethylene is not spherical. Attempts to develop a theoretical description of the dynamics in fluids of non-spherical molecules have been made for many years. The model which most closely corresponds to the molecular shape of ethylene is the prolate spherocylinder. Curtiss and Muckenfuss (32) developed a kinetic theory for non-spherical molecules in the dilute gas region and applied it to the calculation of the diffusion coefficient of a spherocylinder in this region (33). They showed that diffusion in a spherocylinder fluid is faster than in a fluid composed of spheres of the same volume as the spherocylinder. In a limited molecular dynamics study (34) the values of the self-diffusion coefficient at two different densities in the intermediate region for a spherocylinder of length-to-breadth ratio equal to one were calculated. More extensive calculations have been made of the equations of state, compressibility ratios and virial coefficients for a variety of length-to-breadth ratios for spherocylinders (35-37). However, due to the lack of any complete theoretical description or molecular dynamics data for the density dependence of diffusion in a spherocylinder fluid with the ethylene length-to-breadth ratio, we used hard sphere theory to interpret our data.

#### Self-Diffusion in Compressed Supercritical Toluene-d<sub>8</sub>

Our investigation was motivated by the interest in supercritical toluene as a solvent in the extraction of thermally generated coal liquids (38,39). Typically, coal is heated to temperatures between 350° and 450°C in the presence of a supercritical fluid at a pressure of 100-200 atm. As the large molecular weight components depolymerize thermally, the resulting hydrogen rich material dissolves in the supercritical solvent and is removed. Toluene is a convenient solvent to use for the extraction, as its critical temperature is 319°C, and critical pressure is 41 atm. Recent experimental studies of supercritical fluid extraction in the process of coal liquefaction investigate the basic steps involved by varying solvents, pressure and temperatures (40). The goal of our experiment was to provide fundamental data on transport in supercritical toluene-d<sub>8</sub>. These data should help in the design and interpretation of extraction processes using supercritical toluene.

We have measured the self-diffusion coefficient in supercritical toluene-d<sub>8</sub> for temperatures from 300°C to 450°C ( $0.97 \leq T_r \leq 1.22$ ) for pressures of 100, 500 and 1000 bar.

Self diffusion coefficients of deuterated toluene were measured, rather than protonated toluene in order to minimize the experimental difficulties associated with very long proton spin lattice relaxation times ( $T_1$ ). Since the value of the  $T_1$  determines the length of time between pulse sequences, a long relaxation time leads to prohibitively long measurement times. Previous measurements (41-43) of proton and deuterium relaxation times in liquid toluene have been made as a function of temperature and pressure. The relaxation is due to dipolar interactions in protonated toluene and quadrupolar interactions in toluene-d<sub>8</sub>. Therefore, the relaxation times can be expected to increase with increasing temperature. However, the quadrupolar relaxed deuterium  $T_1$  values are smaller than the proton  $T_1$  values, resulting in a comparatively shorter measurement time. The self diffusion coefficients of deuterated toluene should not be significantly different from those of protonated toluene at the temperatures of the measurement and will provide an excellent estimate.

Our previous study (16) of self diffusion in compressed supercritical water compared the experimental results to the predictions of the dilute polar gas model of Monchick and Mason (44). The model, using a Stockmayer potential for the evaluation of the collision integrals and a temperature dependent hard sphere diameters, gave a good description of the temperature and pressure dependence of the diffusion. Unfortunately, a similar detailed analysis of the self diffusion of supercritical toluene is prevented by the lack of density data at supercritical conditions. Viscosities of toluene from 320°C to 470°C at constant volumes corresponding to densities from  $\rho/\rho_c = 0.5$  to 1.8 have been reported (45). However, without PVT data, we cannot calculate the corresponding values of the pressure.

The diffusion data at 100 bar are compared to values obtained using various estimation schemes for the self diffusion coefficient of protonated toluene. No attempt was made to estimate coefficients at 500 and 1000 bar, as these correspond to reduced pressures ( $P_r = 11.9$  and  $24.7$ ) well beyond the range of the approximative methods.

#### Naphthalene Solubility NMR Measurements in Supercritical Carbon Dioxide

We have completed our study of naphthalene solubilities in supercritical carbon dioxide (9). Our unique, in situ NMR method has been used to obtain solubility data for this system at 50.0, 55.0 and 58.5°C in the pressure range of 120-500 bar. Although this system had been previously investigated (46) we have defined better the solubilities near the upper critical end point of the binary mixture. And finally, we have completed our determination of the three phase solid-liquid-vapor curve of the system.

We have developed our static NMR method for the determination of solid solubilities in supercritical fluids. Using this technique we found our 55°C solubility data to agree to within 5% of that taken by Paulaitis, et al. (46), with their technique. We have since proceeded to take data along the previously uninvestigated 50.0 and 58.5°C isotherms. A number of interesting features can be noted. First, by extending the pressure range to 500 bar we were able to observe the limiting solubilities at these isotherms, an effect not before seen for this system. Secondly, the isotherms cross at about 160 bar showing the presence of the two critical end points for the naphthalene/carbon dioxide system. And finally, the 58.5°C isotherm shows a point of inflection at about 235 bar. This behavior shows the close proximity to the upper critical end point (UCEP) temperature and pressure.

The location of the UCEP is quite important to supercritical solubilities, as this critical point gives the maximum temperature at which solid-gas equilibrium exists at all pressures. We have also developed an NMR method to determine for the first time the  $S_2LG$  phase line for this mixture. Since this phase line is terminated by the UCEP, with this data and the inflection point in the  $58.5^\circ\text{C}$  isotherm we can now locate the UCEP at  $60.1^\circ\text{C}$  and 235 bar. Our determination of the UCEP location is about  $3^\circ\text{C}$  lower than that reported previously by Paulaitis, et al. (46). However, the in situ nature of our NMR method allows us to precisely measure this UCEP temperature since we can determine the  $S_2LG$  phase line. These results indicate that our NMR technique can be greatly advantageous for solubility determinations near the UCEP. A more detailed analysis of our experimentally determined solubility data is now in progress.

#### Density and Temperature Effects on Collision Induced Scattering in Supercritical $\text{CO}_2$

In view of the importance of  $\text{CO}_2$  in supercritical fluid extraction, we carried out an experimental study of the pressure and temperature effects on depolarized Rayleigh lineshapes in supercritical  $\text{CO}_2$  (47). Collision induced scattering (CIS) is of considerable interest because it is a fairly unique probe of intermolecular interactions. Depolarized Rayleigh spectra (DRS) of dense atomic fluid and the DRS of spherical molecules have been extensively studied because the entire DRS of these fluids may be attributed to collision induced effects. For linear triatomics the interpretation of the DRS is necessarily more complicated as the time dependence of the polarizability anisotropy of the molecule will contain contributions from both the permanent anisotropy of the molecule, whose time dependence arises from molecular reorientation, and the induced polarizability which arises from multi-body interactions. The part arising from the permanent anisotropy may be referred to as the allowed part and the induced component as the non-allowed part. Despite these complications, significant progress has been made in the study of collision induced effects on the DRS of linear triatomics.

The results of our study were as follows. We obtained experimental data on the density dependence of the DRS of carbon dioxide at temperatures both above and below the critical temperature. By using Madden's theories (48-51) and the analogous results from other linear triatomics [ $\text{CS}_2$ ,  $\text{COS}$ ] (17,18) as a guide, we showed the effects of CIS on the DRS of  $\text{CO}_2$ . Lastly, we showed how failure to adequately account for CIS in the DRS of linear triatomics can cause ambiguity in the interpretation of the information on molecular reorientation present in the DRS.

#### Acknowledgments

This work was partially supported by the Department of Energy under Grant DE-FG-82PC50800.

#### References

1. C. A. Irani and E. W. Funk, in "Recent Developments in Separation Science," N. N. Li, Ed., CRC Press, Cleveland, Ohio, 1977, v. 3A, p. 171.
2. D. F. Williams, Chem. Eng. Science 36, 1769 (1981);
3. G. M. Schneider, Angew. Chem. Int. Ed. 17, 716 (1978).
4. G. Brunner and S. Peter, Ger. Chem. Eng. 5, 181 (1982).
5. J. Jonas, Science 216, 1179 (1982).
6. "Pressure - An Essential Experimental Variable in Spectroscopic Studies of Liquids," J. Jonas in "Phenomena Induced by Intermolecular Interactions," Ed. G. Birnbaum, Proceedings of NATO Advanced Workshop, Bonas, France, 1983; Elsevier, 1984.
7. E. S. Baker, D. R. Brown and J. Jonas, J. Phys. Chem. 88, 5425 (1984).
8. E. S. Baker, D. R. Brown, D. M. Lamb and J. Jonas, J. of Chem. and Eng. Data 30, 141 (1985).
9. D. M. Lamb and J. Jonas, Manuscript in preparation.

10. J. Jonas, Rev. Sci. Instrum. 43, 643 (1972).
11. D. M. Cantor and J. Jonas, J. Mag. Res. 28, 157 (1977).
12. R. J. Finney, M. Wolfe and J. Jonas, J. Chem. Phys. 67, 4004 (1977).
13. N. J. Trappeniers and K. O. Prins, Physica 33, 435 (1967).
14. W. J. Lamb and J. Jonas, J. Chem. Phys. 74, 913 (1981).
15. D. M. Cantor and J. Jonas, J. Mag. Res. 28, 157 (1977).
16. W. J. Lamb, G. A. Hoffman and J. Jonas, J. Chem. Phys. 74, 6875 (1981).
17. B. Hegemann and J. Jonas, J. Phys. Chem. 88, 5851 (1984).
18. B. Hegemann and J. Jonas, J. Chem. Phys. 82, 2845 (1985).
19. W. F. L. Dick and A. G. M. Hedley, in "Thermodynamic Functions of Gases," F. Din, Ed., Butterworths, London, 1962, v. 2, p. 88.
20. A. Michels and M. Geldermans, Physics 9, 967 (1942).
21. A. Sass, B. F. Dodge and R. H. Bretton, J. Chem. Eng. Data 12, 158 (1967).
22. H. Hamann, H. Richter and U. Zucker, Ber. Buns. Phys. Chem. 70, 1084 (1966).
23. S. Chapman and T. G. Cowling, "Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, Cambridge, 1970, 3rd Ed.
24. B. J. Alder, D. M. Gass and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).
25. J. H. Dymond, Physica 75, 100 (1974).
26. J. Jonas, Ann. Rev. Phys. Chem. 26, 167 (1975).
27. J. Jonas in "NATO ASI on High Pressure Chemistry," H. Kelm, Ed., D. Reidel Publ. Co., Dordrecht, Holland, 1978, p. 65.
28. J. Jonas, Rev. Phys. Chem. Japan 50, 19 (1980).
29. D. Chandler, J. Chem. Phys. 60, 3500, 3508 (1974).
30. M. Wolfe, E. Arndt and J. Jonas, J. Chem. Phys. 67, 4012 (1977).
31. H. C. Andersen, D. Chandler and J. D. Weeks, Adv. Chem. Phys. 34, 105 (1976).
32. C. F. Curtiss and C. Muckenfuss, J. Chem. Phys. 26, 1619 (1957).
33. C. Muckenfuss and C. F. Curtiss, J. Chem. Phys. 29, 1259 (1958).
34. D. W. Rebertus and K. M. Sando, J. Chem. Phys. 67, 2585 (1977).
35. T. Boublík, Adv. Chem. Ser. 204, 173 (1983).
36. P. A. Monson and M. Rigby, Mol. Phys. 35, 1337 (1978).
37. P. A. Monson and M. Rigby, Chem. Phys. Lett. 58, 122 (1978).
38. J. C. Whitehead and D. E. Williams, J. Inst. Fuel 48, 397 (1975).
39. N. Berkowitz, "An Introduction to Coal Technology," Academic Press: New York, 1979.
40. W. Worthy, Chem. Eng. News 61, 35 (1983).
41. H. J. Parkhurst, Y. Lee and J. Jonas, J. Chem. Phys. 55, 1368 (1971).
42. D. J. Wilbur and J. Jonas, J. Chem. Phys. 55, 5840 (1971).
43. D. J. Wilbur and J. Jonas, J. Chem. Phys. 62, 2800 (1975).
44. L. Monchick and E. A. Mason, J. Chem. Phys. 35, 1676 (1961).
45. A. Knappwost, F. Ruhe, M. Raschtl, H. Wochnowski and U. Ankara, Z. Phys. Chem. (Wiesbaden) 122, 143 (1980).
46. M. E. Paulaitis and M. McHugh, J. Chem. Eng. Data 25, 326 (1980).
47. K. Baker and J. Jonas, Manuscript in preparation.
48. T. I. Cox, M. R. Battaglia and P. A. Madden, Mol. Phys. 38, 1539 (1979).
49. T. I. Cox and P. A. Madden, Chem. Phys. Lett. 41, 188 (1976).
50. P. A. Madden and T. J. Cox, Mol. Phys. 43, 287 (1981).
51. P. A. Madden and D. J. Tildesley, Mol. Phys. 49, 193 (1983).