Energy

F
O
S
S
I
L

190
10/1/84
(LB)

(1)

~~DR-0440-S~~

DOE/PC/50800-T5
(DE84006591)

DR-0440-S

TRANSPORT AND RELAXATION PROCESSES IN
SUPERCRITICAL FLUIDS

Technical Progress Report for the Period
October 1—December 31, 1983

By
Jiri Jonas

Work Performed Under Contract No. FG22-82PC50800

University of Illinois
Urbana, Illinois

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A02
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

Technical Progress Report
for the Grant Period
10-01-83 to 12-31-83

Project: DE-FG22-82PC50800
"Transport and Relaxation Processes
in Supercritical Fluids"

University of Illinois, Urbana-Champaign Campus
Urbana, Illinois 61801

PRINCIPAL INVESTIGATOR

Name: Jiri Jonas Department: Chemistry
Signature: *Jiri Jonas* Address: 166 Roger Adams Lab
Title: Professor Telephone No.: (217) 333-2572
Social Security Number: 331-40-6560

MASTER

TABLE OF CONTENTS

1. Introduction
2. Theoretical Interpretation of the Experimental Data on Diffusion in Supercritical Ethylene
3. Continued Work
 - 3.1 Testing and Revision of NMR Probe for Solubility Measurements
 - 3.2 Installation and Testing of High Pressure Densitometer for Supercritical Fluids
 - 3.3 Collision Induced Scattering in Supercritical Sulfur Hexafluoride
4. Manuscripts in Preparation

1. Introduction

Our work has continued according to our initial research plans in three main areas: 1) Instrumentation for solubility measurements of solids in supercritical fluids; 2) Transport in supercritical fluids; and 3) Laser Raman scattering studies of collision induced scattering. These experiments yield direct information about intermolecular forces.

2. Theoretical Interpretation of the Experimental Data on Diffusion in Supercritical Ethylene

We have now completed the analysis of the density and temperature dependence of self-diffusion in dense supercritical ethylene. As seen in Fig. 1, the variation in the self-diffusion coefficient is primarily determined by the changes in density over a wide range. The temperature dependence is not significant within the error of the measurements ($D \pm 5\%$). The data cover a range of densities $0.34 < \rho/\rho_c \leq 2.55$ and temperatures $1.14 \leq T/T_c \leq 1.41$.

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 ($T_c = 9.4^\circ\text{C}$). In addition, it is relatively inexpensive and is readily available. Highly accurate compressibility data are available in the literature over a wide range of temperatures and pressures. These data are necessary for a complete analysis of the data. In addition, we plan to study some supercritical fluid mixtures. One of the few mixtures for which density data are available in the literature is ethylene-carbon dioxide. Before any work is done on the mixtures, however, the pure components need to be well characterized. A complete study of the dynamics of pure ethylene is therefore needed. Analysis of the results of the study of ethylene-carbon dioxide mixtures is in progress and will be discussed in our next report.

The density dependence of the ethylene self-diffusion coefficients was analyzed using the Enskog theory of hard spheres corrected for the effects of correlated motion.

FIG. 1

The corrected Enskog theory considers only repulsive forces between molecules, but it has proved to be in excellent agreement with experiments for the transport coefficients of dense gases such as argon, krypton, methane and carbon tetrafluoride for temperatures and pressures above critical. At densities less than critical, the attractive forces between the molecules become important and deviations from the theory are observed.

One of the major difficulties in applying the corrected Enskog theory to experimental data is that accurate hard sphere diameters must be known. We have determined the ethylene diameters in two ways; from the density dependence of the experimental diffusion data, and from the compressibility data. We can then compare the results of the two methods to get an idea of the accuracy of the calculated diameters. The agreement between the two methods is very good. As expected, the diameters obtained from the diffusion data do not show the usual decrease with increasing temperature; this is due to the fact that the errors in the data mask the effect of changing the temperature. However, the compressibility data is much more precise, and therefore, we do see the effective diameter decreasing with increasing temperature, due to the "softness" of the actual repulsive potential.

The hard sphere diameters were then used to calculate the theoretical Enskog coefficients at each density and temperature. The results are shown in Fig. 2, as plots of the ratio of the experimental to calculated coefficients vs. the packing fraction, along with the molecular dynamics results for comparison.

The agreement between the calculated ratios and the molecular dynamics results is excellent at the intermediate densities, especially for those ratios

Δ - σ FROM DIFFUSION DATA
 $\circ$ - σ FROM PVT DATA

FIG. 2

calculated with diameters determined from PVT data. Discrepancies at the intermediate densities can be easily accounted for by errors in measured diffusion coefficients and calculated diameters. The corrected Enskog theory of hard spheres gives an accurate description of the self-diffusion in supercritical dense ethylene.

The biggest differences are obtained for the lower ($\rho \leq \rho_c$) density points at each temperature, where the calculated ratios are up to approximately 20% smaller than the molecular dynamics results. This result is not surprising; at the lower densities, the effects of attractive forces become important and cause diffusion in a real gas to be slower. Dymond has found that the theory predicted the experimental self-diffusion coefficients for densities down to about $0.7 \rho_c$ for $T > T_c$.

We can attempt to correct for the effects of attractive forces using a method used previously by Jonas, et. al. for the analysis of angular momentum correlation times in supercritical CF_4 and CF_4 mixtures with argon and neon. The correction was successfully used to extend the rough hard sphere model to the intermediate and low density regions. When the correction is applied to the calculation of self-diffusion coefficients in supercritical ethylene, however, the corrected values are much smaller than the observed values at all temperatures. The correction overestimates the importance of attractive forces on the value of the diffusion coefficients. Diffusion is thus primarily determined by the repulsive forces between molecules, even at the lowest densities.

The main results of the study may be summarized as follows:

1) The variation of the self-diffusion coefficient in supercritical ethylene is primarily determined by the changes in the density; the temperature dependence is not significant.

2) Molecular hard sphere diameters calculated from diffusion data and PVT data are in good agreement. The temperature dependence σ obtained from PVT data compares well with that observed for other molecules, and the volumes obtained compare well with those obtained from studies modelling ethylene as a spherocylinder.

3) The Enskog theory of self-diffusion of hard spheres provides an excellent description of the density dependence of self-diffusion in supercritical ethylene. Deviations from the theory at densities less than the critical density are attributed to the effects of attractive forces which are not accounted for in the Enskog theory.

3.1 Testing and Revision of NMR Probe for Solubility Measurements

In this quarter the design was perfected and the machining completed for the NMR solubility determination cell (designed for use in the mixing-equipped pressure vessel). The pressure vessel and mixing probe apparatus was assembled and pressure tested in preparation for measurement. In addition, a preliminary experiment in NMR solubility determination without the use of mixing was planned.

The original sketch for the NMR solubility determination cell (see Technical Progress Report 01-01-83 to 03-31-83, Fig. 2) has been improved upon in several important respects (see Fig. 3). The design has been simplified so as to improve machinability and mechanical reliability. This was accomplished by separating the lower support from the cell housing and through choice of tough and resilient plastic materials. Sample volume has been increased to improve NMR sensitivity. The reproducibility of the sample volume, essential to measurement precision, has been improved by shouldering the sample piston (J) on the wall of the sample cell and by relating the maximum travel of the mixing piston (D) to the sample cell through a fixed threaded shaft (P). Machining is complete and the cell is ready for final assembly.

The pressure vessel and mixing apparatus have been assembled and are still being tested. Refinements in the mixing drive have required some further machine shop work which is not yet complete. The pressure vessel has successfully undergone a complete round of pressure testing. This involved burying the vessel in sand (to absorb the shock of a rupture) and pressurizing it through several cycles of varying duration to pressures as much as four times the routine operating pressure. The pressure seal was completely successful both with silver-plated inconel sealing rings and with solvent-resistant (Viton) rubber O-rings.

FIG. 3

NAME OF UNIT S.V.F. - TEST CELL			Don B. Brown Fig. 3 USED WITH CAT-A SEE LARGE ASSEMBLY CAT-A DRAWING NO. S-L-52
DRAWN BY W. H.	DATE 12-15-53	NO. REQ'D 1	
CHECKED BY D.B.	DATE	MATERIAL	
TOLERANCE 3-PLACE DECIMALS $\pm .003$ 2-PLACE DECIMALS $\pm .01$		SCALE FULL	

Since the primary solubility work is delayed during development of the mixing drive, plans have been made for preliminary high pressure NMR solubility studies without mixing. Indications are that this should be possible with a simple modification of the supercritical fluids probe designed earlier by us for studies of supercritical ethylene. These preliminary studies should allow us to prove the NMR technique and guide us in our more extensive measurements to follow.

3.2 Installation and Testing of High Pressure Densitometer for Supercritical Fluids

In the last quarterly report we described the design of a new densitometer (see Fig. 4) capable of precise measurement of p-V-T relations in gases, liquids, and supercritical fluids. The required machine shop work, assembly, installation, and testing have now been completed.

Machining and assembly involved three major components. The first is a massive heat-treated steel pressure vessel and the required support housing. The second component is the sample assembly, which includes a flexible stainless-steel bellows, a pressure vessel plug, and associated high pressure valves for sample handling. The third component is a micrometer assembly which determines the displacement of the bellows and thereby detects changes in sample volume. The bellows, high pressure valves, and micrometer were available commercially; all other parts were produced by the School of Chemical Sciences machine shop.

These parts have now been assembled and installed in our laboratory. Complete installation required connection to our hydraulic pressurization system, connection to the high pressure sample loading system, and assembly of the temperature regulation and measurement equipment. Since safety is such an important consideration in high pressure research, extensive testing was performed

FIG. 4

on the high pressure vessel and all exposed valves and connections. For testing purposes the pressure vessel was buried in sand, filled with an inert pressurizing oil, and pressure-cycled to pressures well above ordinary operating pressures. Results of these safety tests were all positive and the densitometer is now ready for calibration and routine operation.

3.3 Collision Induced Scattering in Supercritical Sulfur Hexafluoride

Collision induced light scattering was studied for dense sulfur hexafluoride at temperatures both above and below the critical temperature ($T_c = 45^\circ\text{C}$). The effects of temperature ($T = 23^\circ\text{C}$ to $T = 125^\circ\text{C}$) and density ($\rho = 1.0 \text{ g/cm}^3$ to 1.9 g/cm^3) were studied independently.

As in the case of supercritical methane, the low frequency portion of the spectra is attributed to the dipole induced dipole (DID) effect. The high frequency collision induced rotational Raman (CIRR) region observed in methane is not distinctly observed in the spectra of sulfur hexafluoride. This is due to the fact that the CIRR region in SF_6 will be less intense due to the higher symmetry of octahedral sulfur hexafluoride.

The spectra are characterized by an exponential decay constant Δ defined by

$$I(\omega) \propto e^{-\omega/\Delta}$$

The experimental decay constants are compared to the values calculated from the theory of Balucani and Vallauri and that of Guillot et. al. Again, as in the case of methane, (see report for the grant period 07-01-83 to 10-01-83) the theory of Balucani and Vallauri was shown to give good agreement with experiment, whereas the theory of Guillot et. al. did not. Figure 5 shows a comparison of the theoretical predictions of Balucani and Vallauri (dashed lines) with experiments to illustrate this agreement.

FIG. 5

4. Manuscripts in Preparation

- 1) E. Baker and J. Jonas, Self-Diffusion in Supercritical Ethylene
- 2) D. Brown, D. Lamb, E. Baker and J. Jonas, Self-Diffusion in Compressed Supercritical Toluene
- 3) K. Baker and J. Jonas, Density Effects on Collision Induced Depolarized Rayleigh Scattering in SF₆
- 4) K. Baker, T. Zerda and J. Jonas, Collision Induced Depolarized Rayleigh Scattering in Supercritical Methane