J. Chem. Eng. Data **1985**, *30*, 141–143

Self-Diffusion in Compressed Supercritical Toluene-d_8

Ellen S. Baker, Donald R. Brown,[†] Douglas M. Lamb, and Jiri Jonas*

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

The self-diffusion coefficients of supercritical toluene-d_8 were measured by using the NMR spin-echo technique for temperatures from 300 to 450 °C at constant pressures of 100, 500, and 1000 bar. The results at 100 bar are compared to the predictions for toluene diffusion by using various empirical correlation methods for estimation of the diffusion coefficients in the supercritical region.

Introduction

Information on the physical properties of supercritical fluids and supercritical fluid mixtures is currently in great demand. A better understanding of the behavior of fluids at supercritical conditions is necessary. The lack of fundamental data on systems of current commercial and theoretical interest makes it difficult to interpret experimental observations. In this paper, we present the results of our experiments on the temperature and pressure dependence of self-diffusion in supercritical toluene-d_8.

Our investigation was motivated by the interest in supercritical toluene as a solvent in the extraction of thermally generated coal liquids (*1*, *2*). 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 (see Table I). Recent experimental studies of supercritical fluid extraction in the process of coal liquefication investigate the basic steps involved by varying solvents, pressures, and temperatures (*4*). The goal of our experiment was to provide fundamental data on transport in supercritical toluene-d_8. 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_8 at constant pressure for temperatures from 300 to 450 °C ($0.97 \leqslant T_r \leqslant 1.22$) 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 (*5*–*7*) 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_8. 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.

Table I. Molecular Constants for Toluene[a]

mol wt	92.141
critical temp, K	591.7
critical press., atm	40.6
critical vol., cm^3/g-mol	316

[a] Reference *3*.

Our previous study (*8*) of self-diffusion in compressed supercritical water compared the experimental results to the predictions of the dilute polar gas model of Monchick and Mason (*9*). The model, using a Stockmayer potential for the evaluation of the collision integrals and a temperature-dependent hard-sphere diameter, 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 to 470 °C at constant volumes corresponding to densities from $\rho/\rho_c = 0.5$ to 1.8 have been reported (*10*). However, without *PVT* data, we cannot calculate the corresponding values of the pressure.

The diffusion data at 100 bar are compared to values obtained by 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 approximate methods.

Experimental Section

The self-diffusion coefficients were measured at the deuterium resonance frequency of 9.21 MHz by using a 14.1-kG electromagnet with a wide gap (3.8 in.) to accommodate the high-pressure vessel. The pulsed NMR spectrometer and receiver system are described in detail elsewhere (*11*). The argon-pressurized, high-pressure, high-temperature NMR probe (*12*) was used previously for studies of relaxation (*13*) and diffusion (*8*) 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 6-ft impedance transforming coaxial cable terminated with a tapped-parallel capacitor box with both fixed and variable capacitors totaling 70 pF in series and 10 pF in parallel. The observed signal peak to rms noise ratio in liquid toluene-d_8 (30 °C) was 60:1 after one scan.

The spectrometer is automated for the measurement of self-diffusion coefficients (*14*) by the Hahn spin-echo sequence (*15*) (90°–τ–180°–τ–echo), with a fixed field gradient. The echo amplitude is measured at six τ values with the magnetic field gradient on and off. The diffusion coefficient is determined from the slope of ln (A_{on}/A_{off}) vs. τ^3 and the known value of the field gradient. The gradient was calibrated at 1 G/cm by

---

[†] Present address: The Procter and Gamble Co., Miami Valley Laboratories, Cincinnati, OH 45247.

0021-9568/85/1730-0141$01.50/0

Table II. Experimental Self-Diffusion Data for Compressed Supercritical Toluene-d_8

	diffusion coeff, 10^{-5} cm^2/s					
P, bar	300 °C	325 °C	350 °C	375 °C	400 °C	450 °C
100	28.2	33.4	43.2	50.0	69.1	106
500	17.3	20.9	22.0	26.3		
1000	14.0	15.2	17.2	20.0		

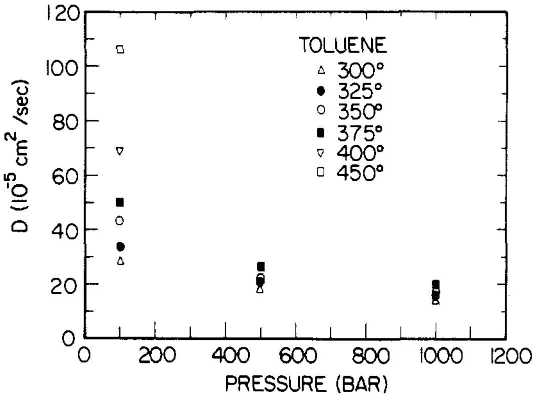

Figure 1. Experimental self-diffusion coefficients of toluene-d_8.

using literature values for the self-diffusion of liquid toluene at room temperature (*16*). It was previously determined (*8*) that although the sample region is heated with an internal furnace, the magnetic field gradient calibration does not change with temperature.

The deuterated toluene samples were obtained from two sources, Alfa Products (Danvers, MA) and Aldrich Chemical Co. (Milwaukee, WI). The samples were rated at better than 99 atom % and were used without further purification.

The error in the measured self-diffusion coefficient varies with the temperature and pressure studied. The estimated accuracy is better than ±10% for all except the lowest density points. For the 400 and 450 °C points at 100 bar, low signal-to-noise ratios lead to estimated errors of ±20%.

Results and Discussion

The results of our measurements of the self-diffusion coefficient in supercritical toluene are given in Table II and displayed in Figure 1. The coefficients were on the order of 10^{-4} cm^2/s, a value typical for compressed supercritical fluids in this range of reduced temperature and pressure. The variation of the diffusion coefficient with temperature and pressure can be explained in terms of the relative changes in density. As the temperature is raised at constant pressure, density decreases and therefore diffusion becomes faster. As pressure is increased at constant temperature, density increases and diffusion slows down. The effect of increasing temperature is more pronounced at lower pressures, since the corresponding density change is greater. At higher pressures, the temperature dependence of the density is not as great, and we do not see a large variation in the diffusion coefficient. This explains the difference in the curvature of the 300 and 375 °C isotherms in Figure 1.

Reasonable success has been achieved in the interpretation of self-diffusion coefficients in compressed supercritical fluids. The Enskog theory of the diffusion of hard spheres (*17*), modified to account for the effects of correlated motion at intermediate and high densities (*18*), has been shown to be in excellent agreement with experimental transport properties of argon, krypton, methane, carbon tetrafluoride (*19*), and ethylene (*20*). However, the effects of attractive forces become apparent for densities less than critical, and the corrected Enskog theory does not reproduce experimental data. The density dependence of the self-diffusion coefficients for compressed supercritical water (*8*), measured over a wide range of temperature ($1.04 \leq T_r \leq 1.50$) and density ($0.315 \leq \rho_r \leq 2.21$), were well described by the dilute polar gas model of Monchick and Mason (*9*).

A detailed analysis of the self-diffusion in supercritical toluene is prevented by the lack of density data at the temperature and pressure conditions of our measurements. Application of the theories mentioned above requires knowledge of both the density and the temperature dependence of the hard-sphere diameter.

Slattery and Bird (*21*) developed a generalized chart for predicting the high-pressure ($P_r \leq 10$) self-diffusion coefficient using Enskog's theory and experimental viscosity and *PVT* data. The chart is convenient to use, as it plots $pD/(pD)^0$ as a function of reduced temperature and pressure, where $(pD)^0$ is the dilute-gas value of the diffusion coefficient, given by (*21*)

$$(pD)^0 = 2.628 \times 10^{-3} \frac{T^{3/2}}{M^{1/2}\sigma^2\Omega_D} \qquad (1)$$

where p is the pressure (atm), D is the diffusion coefficient (cm^2/s), M is the molecular weight, and σ (angstroms) and To_D are the length and collision integral characteristic of the intermolecular potential chosen.

Takahashi (*22*) prepared a similar chart based on experimental values of self-diffusion and binary diffusion coefficients of compressed supercritical gases and gas mixtures. He notes that although the average deviation between the experimental results and the predictions using the generalized chart of Slattery and Bird is 7.9%, these predictions are generally lower than the experimental values. Takahashi's chart gives an average deviation of 4.1% with random scatter of experimental points around the predicted value.

There are several empirical correlations which are suggested for estimating high-pressure diffusion coefficients (*3*). Dawson, Khoury, and Kobayashi (*23*) measured self-diffusion in methane for a wide range of temperatures ($0.8 < T_r < 1.9$) and pressures ($0.3 < P_r < 7.4$). They fitted their data to the equation

$$\rho D/(\rho D)_0 = 1 + 0.053432\rho_r - 0.030182\rho_r^2 - 0.029725\rho_r^3 \qquad (2)$$

with $(\rho D)_0$ the low-pressure value, and ρ_r the reduced density. Mathur and Thodos (*24*) analyzed experimental self-diffusion coefficients for argon, krypton, nitrogen, and carbon dioxide and proposed the relationship

$$\rho_r D = 10.7 \times 10^{-5} T_r/\beta \qquad (3)$$

where

$$\beta = M^{1/2}P_c^{1/3}T_c^{-5/6} \qquad (4)$$

with M the molecular weight, P_c the critical pressure (atmospheres), and T_c the critical temperature (K). The equation reproduced the experimental data for densities up to $\rho_r = 1.5$.

Each of these correlations requires knowledge of the system density. In order to get an idea of how well the above equations predict self-diffusion in supercritical toluene at 100 bar, we can estimate the density values at these conditions by using a three-parameter correlation (P_r, T_r, Z_c) to determine the compressibility factors. The compressibility factors were obtained from generalized $T_r - P_r$ tables (*25*) for a gas with $Z_c = 0.27$. Z_c toluene is 0.264 (*3*). An alternate method (*3*) for determining the compressibility uses the Pitzer acentric factor, ω, as the third parameter for the correlation, rather than the

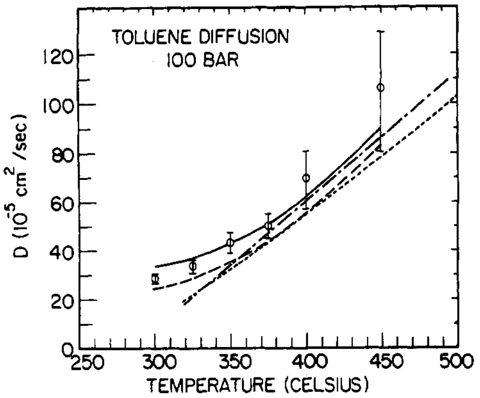

Figure 2. Comparison of experimental diffusion coefficients (O) for toluene-d_8 at 100 bar with predictions for toluene diffusion: (---) method of Slattery and Bird (*21*); (-—-) method of Takahashi (*22*); (— —) method of Dawson et al. (*23*); (—) method of Mathur and Thodos (*24*). The error bars represent differences of plus or minus one standard deviation. See the text for details.

critical compressibility. The results using this method were compared to the results of the first method; no significant differences were observed.

Low-density diffusion values were calculated by using eq 1 with σ, ϵ/k, and the collision integral estimated by using Brokaw's (*26*) relations as described in ref *21*. These equations are based on a Lennard-Jones potential modified to account for toluene's nonzero dipole moment.

The results of these various estimation procedures are shown in Figure 2 along with the experimental results for 100 bar. As expected, the results obtained by using the generalized charts of Slattery and Bird (*21*) and of Takahashi (*22*) do not give a very good agreement with the experimental results. The predicted values are consistently lower than the measured values, and the temperature dependence is not strong enough. The experimental temperature dependence is much more closely reproduced by the more recent empirical correlations of Dawson et al. (*23*) and of Mathur and Thodos (*24*). The exact experimental values are not reproduced by any of the methods. However, considering the difference in molecular weight between toluene and toluene-d_8, the approximations involved, and the error in the experimental values (which gets higher as the density decreases), the correlation of Mathur and Thodos gives a very good estimation of the self-diffusion coefficient in supercritical toluene.

Summary

The self-diffusion coefficient of compressed supercritical toluene has been measured as a function of temperature and pressure. The diffusion coefficients provide fundamental information which is of practical use for engineering applications. The empirical method proposed by Mathur and Thodos gives a good description of the experimental results at 100 bar. More work needs to be done to determine the fundamental physical properties of this important system in order to gain a better understanding of the behavior at supercritical conditions.

Registry No. Toluene-d_8, 2037-26-5.

Literature Cited

(1) Whitehead, J. C.; Williams, D. E. *J. Inst. Fuel* **1975**, *48*, 397.
(2) Berkowitz, N. "An Introduction to Coal Technology"; Academic Press: New York, 1979.
(3) Reid, R. C.; Prausnitz, J. M.; Sherwood, K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977.
(4) Worthy, W. *Chem. Eng. News*. **1983**, *61*, 35.
(5) Parkhurst, H. J.; Lee, Y.; Jonas, J. *J. Chem. Phys*. **1971**, *55*, 1368.
(6) Wilbur, D. J.; Jonas, J. *J. Chem. Phys*. **1971**, *55*, 5840.
(7) Wilbur, D. J.; Jonas, J. *J. Chem. Phys*. **1975**, *62*, 2800.
(8) Lamb, W. J.; Hoffman, G. A.; Jonas, J. *J. Chem. Phys*. **1981**, *74*, 6875.
(9) Monchick, L.; Mason, E. A. *J. Chem. Phys*. **1961**, *35*, 1676.
(10) Knappwost, A.; Ruhe, F.; Raschtl, M.; Wochnowski, H.; Ankara, U. *Z. Phys. Chem*. (*Wiesbaden*) **1980**, *122*, 143.
(11) Jonas, J. *Rev. Sci. Instrum*. **1972**, *43*, 643.
(12) DeFries, T. H.; Jonas, J. *J. Magn. Reson*. **1979**, *35*, 111.
(13) Lamb, W. J.; Jonas, J. *J. Chem. Phys*. **1981**, *74*, 913.
(14) Cantor, D. M.; Jonas, J. *J. Magn. Reson*. **1977**, *28*, 157.
(15) Hahn, E. L. *Phys. Rev*. **1950**, *80*, 580.
(16) Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet*. **1979**, *11*, 705.
(17) Chapman, S.; Cowling, T. G. "Mathematical Theory of Non-Uniform Gases", 3rd ed.; Cambridge University Press: Cambridge, 1970.
(18) Alder, B. J.; Gass, D. M.; Wainwright, T. E. *J. Chem. Phys*. **1970**, *53*, 3813.
(19) Dymond, J. H. *Physica* **1974**, *75*, 100.
(20) Baker, E. S.; Brown, D. R.; Jonas, J. *J. Phys. Chem*., in press.
(21) Slattery, J. C.; Bird, R. B. *AIChE J*. **1958**, *4*, 137.
(22) Takahashi, S. *J. Chem. Eng. Jpn*. **1974**, *7*, 417.
(23) Dawson, R.; Khoury, F.; Kobayashi, R. *AIChE J*. **1970**, *16*, 725.
(24) Mathur, G. P.; Thodos, G. *AIChE J*. **1965**, *11*, 613.
(25) Lydersen, A. L.; Greenkorn, R. A.; Hougen, O. A. *Rep.—Univ. Wis., Eng. Exp. Stn*. **1955** *No. 4*.
(26) Brokaw, R. S. *Ind. Eng. Chem. Process Des Dev*. **1969**, *8*, 240.

Received for review June 22, 1984. Accepted October 22, 1984. This research was partially supported by the Department of Energy under Grant DE-FG-82PC50800.