Diffusion of Benzene, Toluene, Naphthalene, and Phenanthrene in Supercritical Dense 2,3-Dimethylbutane

The conditions under which the Taylor-Aris dispersion phenomenon can be employed to generate accurate tracer diffusion data in supercritical dense fluids are established. The technique is used to determine the diffusivities of benzene, toluene, naphthalene, and phenanthrene in supercritical dense 2,3-dimethylbutane as a function of temperature and pressure. A molecular theory incorporating the Sung-Stell formulation of molecular dynamic correlations in smooth-hard-sphere fluids and the Baleiko-Davis molecular roughness for polyatomics with the Enskog-Thorne dense gas diffusivity relationship is found to represent our experimental data to within ±4%. The values of the effective hard-sphere diameters involved in the present theory can be predicted fairly accurately from the critical volumes of the solutes and solvent considered here.

C. K. J. SUN and S. H. CHEN

Department of Chemical Engineering
University of Rochester
Rochester, NY 14627

SCOPE

Binary diffusivity is an important property in correlating and predicting the mass transfer coefficient for the design of separation processes. Separation using supercritical dense gases has proven to be advantageous over conventional methods such as liquid extraction or distillation, and yet there exist no consistent binary diffusion data for application under such conditions. This study is aimed at providing a reliable experimental method on the basis of the Taylor-Aris dispersion phenomenon. The measured values of the tracer diffusivities of a series of aromatic hydrocarbons in supercritical dense 2,3-dimethylbutane are used to furnish a fundamental understanding of binary diffusion within the framework of a molecular theory.

CONCLUSIONS AND SIGNIFICANCE

We have analyzed the experimental conditions under which the Taylor-Aris dispersion phenomenon can be reliably employed in practice to determine the tracer diffusion coefficient in supercritical dense fluids. On the basis of the Enskog-Thorne dense gas theory, the Sung-Stell formulation of molecular dynamic correlations in smooth spheres, and the Baleiko-Davis theory of rough spheres, the present theory is shown to *represent to within ±4% the observed diffusivities of benzene, toluene, naphthalene, and phenanthrene in supercritical dense 2,3-dimethylbutane at temperatures from 523.2 to 548.2 K and pressures from 5.352×10^6 to 1.590×10^7 N/m^2.* The fact that the effective solute and solvent molecular diameters can be fairly accurately predicted from critical volumes verifies the practical application of the present theory. The theory is also used to reveal the inconsistency and probable lack of accuracy of the existing data for tracer diffusion in supercritical dense carbon dioxide.

INTRODUCTION

Supercritical fluid extraction (SCFE) offers a number of advantages over conventional liquid extraction or distillation (Williams, 1981; Paulaitis et al., 1983). The design of SCFE processes requires a knowledge of molecular diffusivity for correlating and predicting the mass transfer coefficient. Unfortunately, the few binary diffusion data available thus far appear to be inconsistent and probably lack accuracy, as will be discussed below. Thus it is

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Correspondence concerning this paper should be addressed to S. H. Chen.

crucial that a reliable experimental method be established for gathering accurate data before fundamental understanding of diffusion in supercritical dense fluids and correlation development can be accomplished. One of the objectives of this study is to present an experimental technique on the basis of the Taylor-Aris dispersion phenomenon (Taylor, 1953; Aris, 1956). The technique is employed to measure the binary tracer diffusion coefficients of benzene, toluene, naphthalene, and phenanthrene in supercritical dense 2,3-dimethylbutane ($T_c = 500.0$ K, $P_c = 3.14 \times 10^6$ N/m^2), a solvent proven to be desirable for separation under supercritical conditions (Barton and Hajnik, 1980). Conditions for the present diffusion measurements fall in the range of practical interest: $0.9 < T_R < 1.2$ and $P_R > 1$. The other objective is to use the measured values of the diffusion coefficients to test the performance of a hard-sphere theory of diffusion which incorporates Enskog and Thorne's dense-gas relationship (Chapman and Cowling, 1970), Baleiko and Davis's (1974) molecular roughness, and Sung and Stell's (1984) formulation of molecular dynamic correlations present in the dense fluid region. The deficiency of computer simulation results on hard-sphere fluids encountered in dealing with binary diffusion in supercritical dense carbon dioxide (Chen, 1983) is thereby removed.

EXPERIMENTAL

The Taylor dispersion technique employed previously to determine the diffusivity in liquids (Chen et al., 1983) is extended for diffusion measurement in the supercritical dense fluid region by including axial diffusion in the formulation of dispersion coefficient. In other words, the Aris (1956) generalization of the Taylor (1953) dispersion analysis in liquids, together with Levenspiel and Smith's (1957) condition for a Gaussian distribution of solute concentration at tube end, provides the means to calculate binary diffusivity from the observed dispersion:

$$K = D_{12} + \frac{a^2u^2}{48D_{12}} \tag{1}$$

where K is the dispersion coefficient, D_{12} the tracer diffusivity of solute (*1*) in solvent (*2*), u the mean fluid velocity, and a the tube radius. According to Levenspiel and Smith (1957), the concentration distribution at the tube end is Gaussian if

$$\frac{K}{uL} < 0.01 \tag{2}$$

where L is the tube length. According to Giddings and Seager (1962), D_{12} can be calculated from the following expression:

$$D_{12} = \frac{u}{4}\left[H - \left(H^2 - \frac{a^2}{3}\right)^{1/2}\right] \tag{3}$$

in which H, the plate height, can be found from the tube length L, half-height width $W_{1/2}$, and retention time t as follows (Cloete et al., 1976),

$$H = \frac{LW_{1/2}^2}{5.54t^2} \tag{4}$$

Shown in Figure 1 is a schematic diagram of the apparatus constructed for the present research. To get rid of the dissolved air, helium is constantly bubbled through the solvent. The solvent is delivered at room temperature at a low and steady flow rate (typically 6×10^{-6} m^3/h) with a high-performance liquid chromatography metering pump (Constametric III, Milton Roy Co.). A Reodyne valve is used to inject 2×10^{-8} m^3 dilute solution (typically 0.5 wt.%) into the flowing solvent prior to entering the dispersion column. The column is made of 57.79 m long, 1.59×10^{-3} m O.D. and 7.88×10^{-4} m I.D. stainless steel capillary tube coiled in 0.2 m radius. It is submerged in a constant-temperature oil bath that can be heated to 573 K and maintained to within ±0.2 K. The initial dispersion plus volume expansion in the tube length over which the liquid is heated to within 0.1 K of the bath temperature accounts for only 0.3% of the total dispersion length. Using the results of Gill and Sankarasubramanian (1971) as well as those of Evans and Kenney (1965), one finds that such an extent of initial dispersion has a negligible effect on the diffusivity calculated from the observed solute dispersion. After about 3–4 h of dispersion, the fluid is cooled back to room temperature and passes through a section which is constricted to provide a pressure up to 2×10^7 N/m^2 by viscous friction. It is noticed that fluid flow through the constricted section is accompanied by cooling upon volume expansion, which tends to further increase the system pressure by reducing the passage in this section. By maintaining a constant temperature around this section the pressure can be kept constant to within ±0.2% of the value determined by a Heise gauge. The tube length for temperature and pressure reduction is about 0.1% of that of the dispersion column. A UV absorbance detector (Milton Roy Co.) monitors the solute concentration profile. Questions may arise as to the feasibility of coiling the tube and of reducing both temperature and pressure prior to the detector. In fact, the perturbations on the measured diffusivity due to secondary flow can be estimated from the second term of the righthand side of the following equation (Nunge et al., 1972),

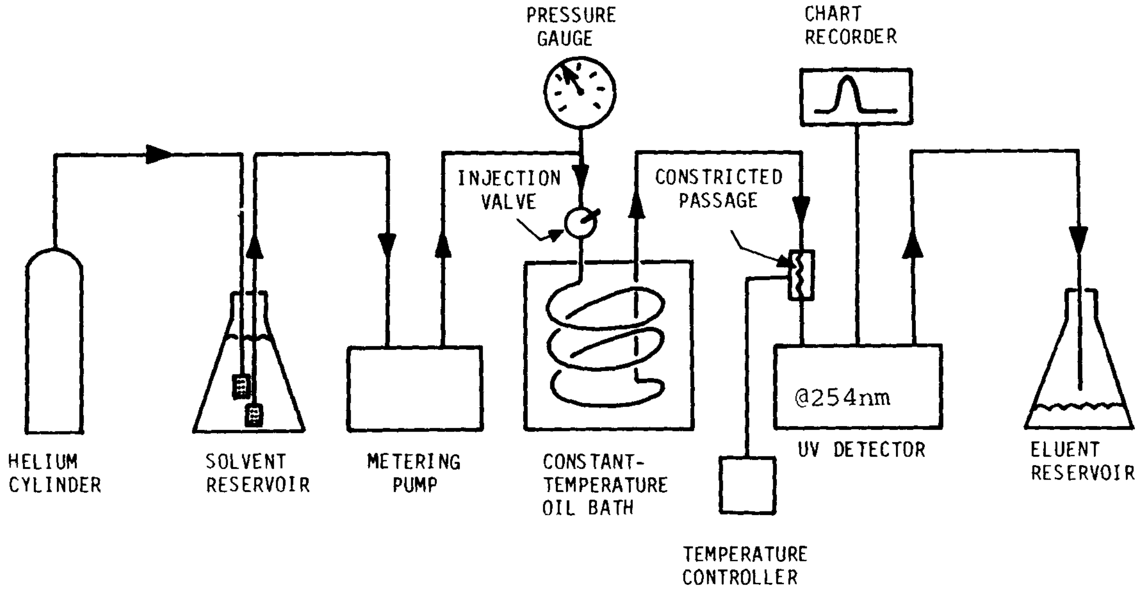

Figure 1. Schematic diagram of the diffusion apparatus.

$$K' = K + (7.54 \times 10^{-8}) D_{12} Pe^2 Re^4 \left(\frac{a}{R}\right)^2 \times [-0.162 Sc^2 + 2.52 \times 10^{-3}] \tag{5}$$

where K' is the dispersion coefficient in coiled tube, K is that in a straight tube given by Eq. 1, R is the coil radius, and Pe, Re, Sc are the Peclet, Reynolds, and Schmidt numbers defined to be

$$\begin{aligned} Pe &= Re \cdot Sc \\ Re &= 2a\rho u/\mu \\ Sc &= \mu/\rho D_{12} \end{aligned} \tag{6}$$

in which ρ is the fluid density and μ the viscosity. The perturbations due to temperature/pressure reduction occurring within a short length between the dispersion column and detector are negligible if the following condition is satisfied (van der Laan, 1958),

$$uL/K \gtrsim 1{,}000 \tag{7}$$

For dense fluids for which the viscosity is on the order of 10^{-5}–10^{-3} N·s/m^2, diffusivity 10^{-9}–10^{-7} m^2/s, density 10^2–10^3 kg/m^3, sample calculations show that with the present experimental apparatus the diffusivity can be obtained from Eq. 3 while neglecting the effects of tube curvature and temperature/pressure reduction prior to detection.

For a typical diffusion measurement, the pump is started to build up pressure before the oil bath is heated. Once both temperature and pressure have reached the desired readings, the flow system is allowed to equilibrate for 3–4 h. Injection of sample solutions then follows at intervals of 15 m. The reproducibility of measured diffusivities is ±2% or better for a total of three to four injections. The retention time of the injected solution pulse is about 3 h. Over a 12 h period the pressure reading is stable to within ±0.5%, while the oil bath temperature is always controlled to within ±0.2 K. Thus, it is believed that our experimental apparatus and procedures are capable of generating accurate diffusion data.

Materials. The solute benzene (99%+), toluene (99%+), naphthalene (99%+) and phenanthrene (98%+), all purchased from Aldrich Chemical Co., and solvent 2,3-dimethylbutane (99%, Alfa) were all used as received, without further purification.

THEORETICAL BACKGROUND

In the treatment of the present diffusion data in the supercritical dense fluid region, the factor $D_{12}{}^{SHS}/D_{12}{}^{E}$ in the rough-hard-sphere equation of molecular diffusion (Chandler, 1974a,b; Baleiko and Davis, 1974), namely,

$$D_{12}^{RHS} = \left(\frac{D_{12}^{SHS}}{D_{12}^{E}}\right) D_{12}^{E} h_{12} \tag{8}$$

is derived from Sung and Stell's (1984) theory of tracer diffusion (i.e., binary diffusion at infinite dilution):

$$\frac{D_{12}^{SHS}}{D_{12}^{E}} = \left(\frac{1 + \gamma_B \dfrac{\sigma_2}{\sigma_1}}{1 + \gamma \dfrac{\sigma_2}{\sigma_1}}\right)^2 \frac{Y_{12}}{1 + 4\xi_2 Y_{22}} + \frac{1 + \dfrac{\sigma_2}{\sigma_1}}{1 + \gamma \dfrac{\sigma_2}{\sigma_1}} \frac{D_{12}^{H}}{D_{12}^{E}} \tag{9}$$

In Eq. 8, $D_{12}{}^{E}$, the Enskog-Thorne tracer diffusivity in the dense gas region, is given by (Chapman and Cowling, 1970):

$$D_{12}^{E} = \frac{3}{8 n_2 \sigma_{12}^2 Y_{12}} \left(\frac{kT}{2\pi m_{12}}\right)^{1/2} \tag{10}$$

where n_2 is the solvent number density, σ_{12} is $(\sigma_1 + \sigma_2)/2$, and m_{12} is $m_1 m_2/(m_1 + m_2)$. In the case of tracer diffusion, the Mansoori-Carnahan-Starling-Leland formula for pair correlation function at contact reduces to (Sung and Stell, 1984):

$$Y_{12} = (1 - \xi_2)^{-3} \left(1 - \xi_2 + \frac{2\xi_2}{1 + \dfrac{\sigma_2}{\sigma_1}}\right) \left(1 - \xi_2 + \frac{\xi_2}{1 + \dfrac{\sigma_2}{\sigma_1}}\right) \tag{11}$$

in which the packing efficiency $\xi_2 = \pi n_2 \sigma_2{}^3/6$. For self-diffusion $\sigma_1 = \sigma_2$, and Eq. 11 further reduces to

$$Y_{22} = \frac{1 - \dfrac{\xi_2}{2}}{(1 - \xi_2)^3} \tag{12}$$

For molecular roughness $h_{12} = 0.714$ is adopted on the basis of uniform mass distribution within the effective hard-sphere volume (Baleiko and Davis, 1974). The effects of collective molecular motion appear in Eq. 9 as $D_{12}{}^{H}$, the diffusivity in the hydrodynamic limit, and γ, the low-density limit of which is γ_B. The value of γ is found numerically for given ξ_2 and σ_2/σ_1 from the following relationship:

$$(1 - \xi_2^*)^{-3} \left(1 - \xi_2^* + \frac{2\xi_2^*}{1 + \dfrac{\sigma_2}{\sigma_1}}\right) \left(1 - \xi_2^* + \frac{\xi_2^*}{1 + \dfrac{\sigma_2}{\sigma_1}}\right) = 1 + \frac{4\xi_2 \left(1 - \dfrac{\xi_2}{2}\right)}{(1 - \xi_2)^3} \tag{13}$$

in which the apparent packing efficiency $\xi_2{}^*$ is defined as $\gamma^3 \xi_2$. The value of γ_B is also found from Eq. 13 at ξ_2 successively reduced from 10^{-5} until the converging value is obtained. The other feature of Eq. 9 is that both hydrodynamic ($D_{12}{}^{H}$) and Enskog-Thorne limits ($D_{12}{}^{E}$) are considered, and the ratio $D_{12}{}^{H}/D_{12}{}^{E}$ turns out to be

$$\frac{D_{12}^{H}}{D_{12}^{E}} = 2.881 \left(1 + \frac{\sigma_1}{\sigma_2}\right)\left(1 + \frac{m_2}{m_1}\right)^{-1/2} \times \frac{\xi_2 Y_{12} Y_{22}}{(\mu_2^{SHS}/\mu_2^{E})(1 + 3.20\xi_2 Y_{22} + 12.18\xi_2^2 Y_{22}^2)} \tag{14}$$

in which $\mu_2{}^{SHS}/\mu_2{}^{E}$, the ratio of smooth-hard-sphere viscosity to the Enskog-Thorne prediction, is formulated as follows using Alder et al's. (1970) computer results in the thermodynamic limit,

$$\frac{\mu_2^{SHS}}{\mu_2^{E}} = 1 + 1.27 \exp[23.78(\xi_2 - 0.5)] \tag{15}$$

In essence, the rough-hard-sphere model carries two parameters, i.e., the effective hard-sphere diameters for solute and solvent molecules. Instead of treating them both as adjustable parameters, we reduce Eqs. 8–14 for self-diffusion by imposing $\sigma_1 = \sigma_2$ and $m_1 = m_2$. Among the solutes and solvent under present investigation, the self-diffusion data as a function of temperature are available only for benzene from 288.2 to 328.2 K (McCool et al.,1972). The values of σ's fitted from observed values of self-diffusivity using Eqs. 8–14 reduced for self-diffusion are then cast in the following form proposed for liquid metals by Protopapas et al. (1973):

$$\sigma(T) = \frac{\sigma_m[1 - B(T/T_m)^{1/2}]}{1 - B} \tag{16}$$

where the subscript m designates the melting point, and B is a numerical constant related to the curvature at the minimum of

TABLE 1. TRACER DIFFUSIVITY OF FOUR SOLUTES IN SUPERCRITICAL DENSE 2,3-DIMETHYLBUTANE, AND COMPARISON BETWEEN THEORY AND EXPERIMENT

Parameter				Diffusivity D ($10^9 D_{12}^{expt}$, m^2/s) and Comparison C ($D_{12}^{RHS}/D_{12}^{expt}$)			
T K	P 10^6 N/m^2	V m^3/kmol		Benzene	Toluene	Napthalene	Phenanthrene
523.2	15.32	0.1876*	D	25.0	23.0	19.9	17.2
			C	0.97	0.98	0.98	0.95
523.2	10.23	0.2000**	D	28.9	26.4	23.0	19.7
			C	0.96	0.97	0.97	0.95
523.2	6.897	0.2222**	D	33.9	30.8	26.5	22.4
			C	1.00	1.02	1.03	1.02
523.2	5.352	0.2500**	D	38.9	—	31.0	25.9
			C	1.07	—	1.08	1.08
535.2	15.90	0.1911*	D	26.6	24.4	21.6	18.3
			C	0.96	0.97	0.95	0.94
535.2	12.44	0.2000**	D	29.0	27.0	—	20.0
			C	0.96	0.96	—	0.94
535.2	8.145	0.2222**	D	35.0	31.3	27.8	23.2
			C	0.98	1.02	0.99	1.00
535.2	6.276	0.2500**	D	40.1	36.8	—	26.6
			C	1.05	1.07	—	1.06
548.2	14.37	0.2000**	D	29.8	28.1	24.0	20.5
			C	0.95	0.94	0.95	0.93
548.2	9.938	0.2222**	D	35.3	32.7	28.1	23.7
			C	0.98	0.99	0.99	0.99
548.2	7.614	0.2500**	D	40.4	38.7	32.1	26.7
			C	1.06	1.02	1.06	1.07

* Molar volume estimated with Benedict-Webb-Rubin-Friend equation of state using coefficients reported for 2,3-dimethylbutane by Griskey and Beyer (1963).

** Molar volume of 2,3-dimethylbutane experimentally determined by Kelso and Felsing (1942).

intermolecular potential. The justification for using Eq. 16 is further discussed below. However, it should be noted that the temperature variation of the effective hard-sphere diameter, as stated by Eq. 16, is accounted for by the balance between the relative kinetic energy and repulsive potential energy of a pair of colliding molecules of a real fluid (Protopapas et al., 1973). The effective hard-sphere diameter of benzene molecule predicted from Eq. 16 at a given temperature is then used to obtain the effective hard-sphere diameter of 2,3-dimethylbutane molecule by fitting the experimental tracer diffusivity to Eqs. 8–15. We also treat the effective hard-sphere diameters of the molecules of the rest of the solutes as adjustable parameters simply because of the lack of self-diffusion data as a function of temperature. For the rather limited temperature range involved in our diffusion measurements, it seems reasonable to neglect the temperature variation of the effective hard-sphere diameters of all substances concerned.

RESULTS AND DISCUSSION

The tracer diffusivities of benzene, toluene, naphthalene, and phenanthrene in supercritical dense 2,3-dimethylbutane determined with the Taylor-Aris dispersion method are presented in Table 1 as a function of temperature and pressure. Each reported diffusivity is the mean of three to four measurements, and the standard deviation is ±2% or better. Also given in Table 1 are the molar volumes of 2,3-dimethylbutane either reported by Kelso and Felsing (1942) or estimated with the Benedict-Webb-Rubin-Friend equation of state using the coefficients reported by Griskey and Beyer (1963). In order to verify the consistency of our data, we plot $\ln(10^9 D_{12})$ against $\ln V_R$ in Figure 2 for the diffusion of four solutes at 523.2 K. It is clear that as the ideal gas limit is approached, the slopes all tend to unity, which is expected of the Chapman-Enskog relationship, i.e., Eq. 10 with $Y_{12} = 1$, and the intercepts reflect the masses and effective sizes of the solute molecules. As the solvent molar volume decreases, both collision transfer (as opposed to molecular transfer) and collective molecular motion become more important, which leads to a sharper decline in the molecular diffusivity. This qualitative behavior is also exhibited by the self-diffusion in methane at a comparable T_R (Dawson et al., 1970) across a wider range of V_R, as plotted in Figure 3. Figure 4 is intended to reveal the inconsistency and probable lack of accuracy of the tracer diffusion data in supercritical dense carbon dioxide reported in the past (Tsekhanskaya, 1971; Swaid and Schneider, 1979; Feist and Schneider, 1982). However, the self-diffusivities of supercritical dense carbon dioxide, (O'hern and Martin, 1955) appear to be reasonable in the sense that the slope approaches 1 as the molar volume increases (see also Figure 4).

To test the performance of the theory presented in the preceding section, we first fit the self-diffusion data for benzene at atmospheric pressure and temperature from 288.2 to 328.2 K (McCool et al., 1972) to Eqs. 8–15 reduced for self-diffusion to

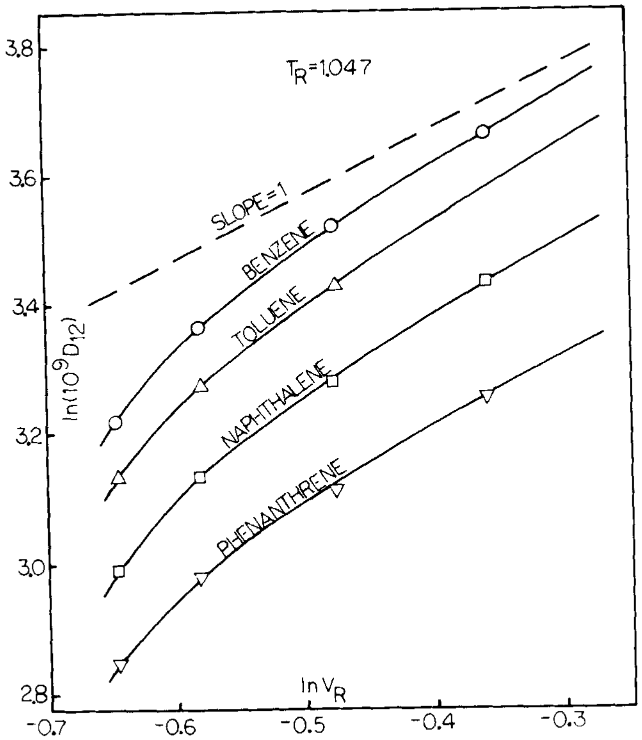

Figure 2. Molecular diffusivity (10^9D_{12}) vs. molar volume (V_R) for tracer diffusion in supercritical dense 2,3-dimethylbutane at 523.2 K.

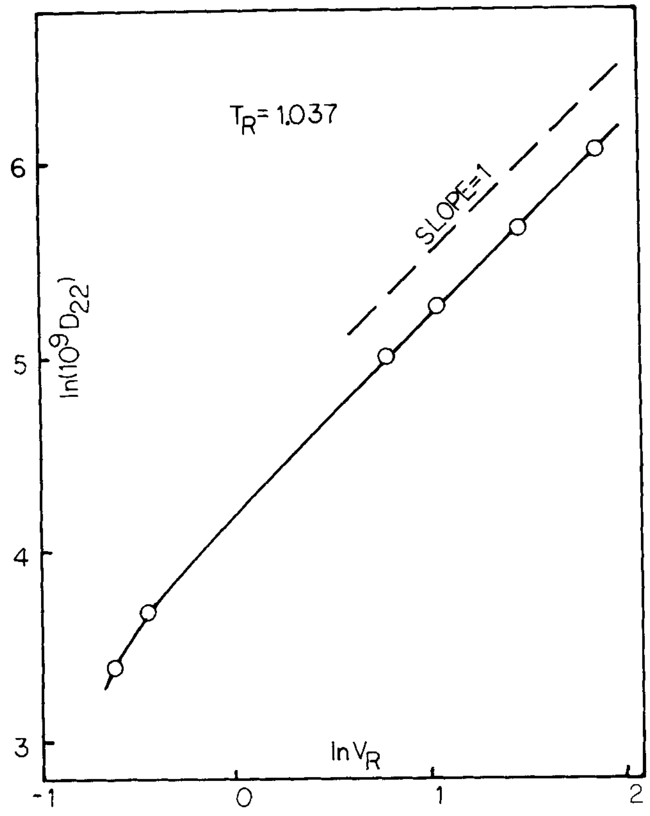

Figure 3. Molecular diffusivity (10^9D_{22}) vs. molar volume (V_R) for the self-diffusion in supercritical dense methane at 197.7 K; data from Dawson et al. (1970).

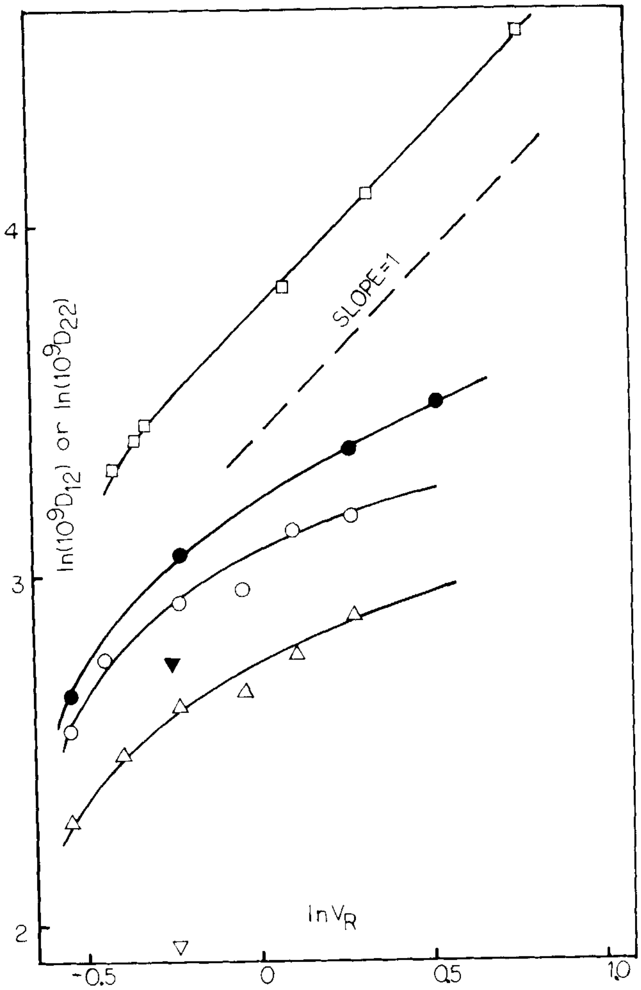

Figure 4. Molecular diffusivities (10^9D_{12}, 10^9D_{22}) vs. molar volume (V_R) for tracer diffusion and self-diffusion in supercritical dense carbon dioxide.

□ Carbon-14 dioxide, 308 K (O'hern and Martin, 1955)
● Benzene, 313 K (Feist and Schneider, 1982)
○ Benzene, 313 K (Swaid and Schneider, 1979)
△ 1,3,5-Trimethylbenzene, 313 K (Swaid and Schneider, 1979)
▼ Naphthalene, 308 K (Feist and Schneider, 1982)
▽ Naphthalene, 308 K (Tsekhanskaya, 1971)

obtain the effective hard-sphere diameters at four temperatures: 288.2 K, 5.19 × 10^{-10} m; 298.2 K, 5.16 × 10^{-10}; 313.2 K, 5.13 × 10^{-10}; and 328.2 K, 5.08 × 10^{-10}. This set of diameters fitted to the form of Eq. 16 yields B = 0.223 and σ_m = 5.21 × 10^{-10} m, the latter being fairly close to the van der Waals radius of 5.36 × 10^{-10} m (Bondi, 1964). Furthermore, the packing efficiency of liquid benzene at the melting point of 278.7 K, where the liquid density is 894 kg/m^3 (Raznjevic, 1976), is found to be $\xi_m = \pi n_m \sigma_m{}^3/6 = 0.511$, which falls in the freezing range of $0.48 \le \xi_m \le 0.54$ predicted for hard-sphere model fluids by Monte Carlo simulations (Hoover and Ree, 1968) and is in excellent agreement with Haymet's (1983) theoretical value of 0.511 for a hard-sphere liquid to freeze under equilibrium conditions. It is also interesting to note that the value of B found here for benzene, 0.223, is reasonably close to that estimated for liquid metals, 0.112, by Protopapas et al. (1973). Hence, one is inclined to claim that the procedure followed here to estimate the effective hard-sphere diameter for a real fluid (such as benzene) is physically sound. Across the temperature range from 523.2 to 548.2 K encountered in our diffusion measurements, the effective hard-sphere diame-

TABLE 2. EFFECTIVE HARD-SPHERE DIAMETERS AND CRITICAL VOLUMES FOR SUBSTANCES INVESTIGATED

Substance	Hard-Sphere Dia., $10^{10}\sigma$ m	Critical Vol., V_c $m^3/kmol$
2,3-Dimethylbutane	5.49	0.358**
Benzene	4.64*	0.359**
Toluene	4.98	0.316**
Naphthalene	5.78	0.410**
Penanthrene	7.00	0.554†

* Predicted with Eq. 16.
** Reid et al. (1977).
† Predicted with Lydersen's group contribution method (Reid et al., 1977).

ter for benzene decreases from 4.66 to 4.61 × 10^{-10} m. The variation is so significant that the mean value, 4.64 × 10^{-10} m, is quite adequate for the present interpretation.

We then proceed to calculate the effective hard-sphere diameter of 2,3-dimethylbutane by fitting the observed tracer diffusivities of benzene (reported in Table 1) to Eqs. 8–15. It turns out that a single value of σ_2, 5.49 × 10^{-10} m, is capable of representing the experimental data to within ±4% on the average; D_{12}^{RHS} predicted with Eq. 8 is compared to D_{12}^{expt} also in Table 1. With the effective hard-sphere diameters for solutes other than benzene as listed in Table 2, the present theory predicts tracer diffusivities again to within ±4% on the average, the maximum deviation being 8%. In addition, it is noted that although the effective hard-sphere diameters are all treated as adjustable parameters except for benzene, their values follow the trend of critical volumes, as also demonstrated in Table 2. The values of V_c's are all taken from Reid et al. (1977) except for phenanthrene for which V_c is estimated to be 0.554 $m^3/kmol$ with Lydersen's group contribution method, which has proven to be the most accurate of the several methods surveyed by Klincewicz and Reid (1984) for the series of aromatic hydrocarbons considered here. It is thus legitimate to conclude that the present theory is quite adequate for describing the tracer diffusion in supercritical dense fluids. To facilitate practical applications of the theory we represent the linear correlation between σ and $V_c^{1/3}$ (shown in Figure 5) as:

$$10^{10}\sigma(m) = 13.03\ V_c^{1/3}\ (m^3/kmol) - 3.78 \qquad (17)$$

for the five substances of interest here. The effective hard-sphere diameters obtained with Eq. 17 predict diffusivities that deviate from observed values to within ±4% on the average. We note in passing that the intercept in Eq. 17 reflects the void space between molecules of real fluids at the critical point.

ACKNOWLEDGMENT

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

NOTATION

a = tube radius, m
B = a parameter in Eq. 16, dimensionless
D = molecular diffusivity, m^2/s
H = plate height, m
h = roughness factor, 0.714
K = dispersion coefficient, m^2/s
k = Boltzmann's constant 1.38 × 10^{-23} J/K.
L = tube length, m

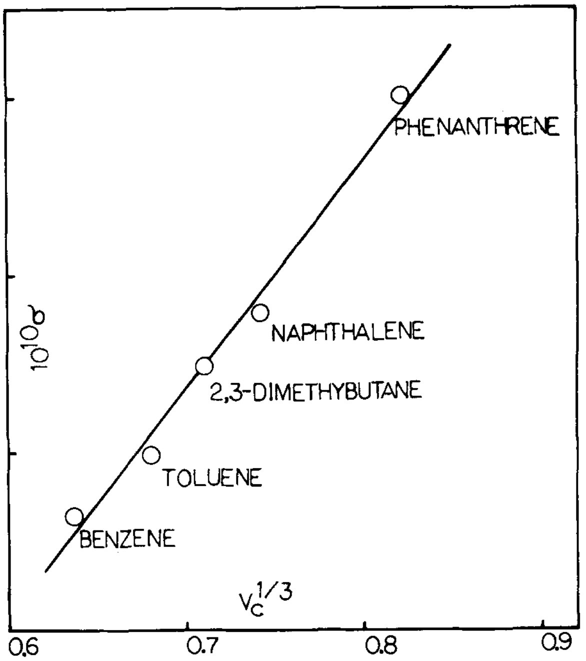

Figure 5. Correlations between effective hard-sphere diameter σ and critical volume V_c.

m = molecular mass, kg
n = number density, m^{-3}
P = pressure, N/m^2
Pe = Peclet number ≡ Re·Sc
R = coil radius, m
Re = Reynolds number ≡ $2a\rho u/\mu$
Sc = Schmidt number ≡ $\mu/\rho D_{12}$
T = absolute temperature, K
t = retention time, h
u = mean fluid velocity, m/s
V = molar volume, $m^3/kmol$
$W_{1/2}$ = half-height, width, h
Y = pair correlation function at contact, dimensionless

Greek Letters

ρ = fluid density, kg/m^3
μ = fluid viscosity, $N \cdot s/m^2$
σ = effective hard-sphere diameter, m
γ = size factor accounting for the collective motion of solvent molecules
γ_B = γ in the low-density limit
ξ = packing efficiency, dimensionless
ξ^* = defined as $\gamma^3\xi$, dimensionless

Superscripts

E = Enskog-Thorne limit
H = hydrodynamic limit
RHS = rough-hard-sphere value
SHS = smooth-hard-sphere value
$expt$ = experimental value

Subscripts

1 = solute
2 = solvent
12 = tracer diffusion of 1 in 2
22 = self-diffusion in solvent

c = critical property
m = melting point
R = reduced property

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Manuscript received Aug. 16, 1984; revision received Jan. 21, and accepted Jan. 25, 1985.