Tracer Diffusion of Aromatic Hydrocarbons in Liquid Cyclohexane Up To Its Critical Temperature

Tracer diffusion coefficients in liquid cyclohexane of benzene, toluene, *p*-xylene, mesitylene, naphthalene, and phenanthrene have been determined from 298.2 to 523.2 K (T_R = 0.54 ~ 0.95) using the Taylor dispersion method. Positive deviations from the Arrhenius relationship are observed as the critical temperature is approached, but a rough-hard-sphere theory is found to be adequate for describing the data across the entire temperature range. On the basis of the computer simulation results for hard-sphere fluids, correlations involving solute and solvent critical volumes and their molecular weights have also been developed for practical applications. Tracer diffusivities in supercritical carbon dioxide are also adequately represented by the proposed correlation, as the fluid density is not far removed from that of liquid carbon dioxide.

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SCOPE

The design of chemical reactors or separation processes often requires a knowledge of binary diffusion coefficients. In particular, current advances in separation technology using dense fluids as solvents have resulted in a need for diffusion data in the range $0.9 < T_R < 1.2$ and $P_R > 1.0$. (Paulaitis et al., 1983). In view of the absence of experimental data on binary diffusion in liquids up to the critical point, we have determined the tracer diffusivities of a series of aromatic hydrocarbons in liquid cyclohexane up to $T_R = 0.95$ using the Taylor dispersion method. The results are used to test the performance of a rough-hard-sphere theory as well as the Arrhenius equation and to generate correlations to improve prediction accuracy.

CONCLUSIONS AND SIGNIFICANCE

The Taylor dispersion method has been employed to generate new tracer diffusion data in liquids up to their critical temperatures. Using measured values of tracer diffusivities in liquid cyclohexane of benzene, toluene, *p*-xylene, mesitylene, naphthalene, and phenanthrene, we have demonstrated the success of a rough-hard-sphere theory. It has also been shown that there are positive deviations from the Arrhenius equations as the critical temperature is approached, which is consistent with what has been observed for the self-diffusion of liquid normal alkanes up to their critical temperatures (Panchenkov et al., 1969). An extension of Dymond's hard-sphere self-diffusion equation, which was developed using the results of molecular dynamics computation results for an infinite number of hard spheres, predicts a linear relationship between $D_{12}/\sqrt{T}$ and V/V_o up to the critical temperature. A second correlation which explicitly accounts for the solute and solvent molecular mass and size discrepancies, has also been established using the results of computer simulations for the tracer diffusion in a finite number of hard spheres. When the solute and solvent critical volumes are used as parameters (instead of effective hard-sphere diameters), both correlations developed above are capable of representing the present diffusion data to within ±4% on the average with a maximum error of 13%. In contrast, the Wilke-Chang equation predicts tracer diffusivities which deviate from presently reported values by ±17% on the average, the maximum error being 40% at the highest temperature. Additional diffusion data collected from the literature, including the tracer diffusivities of benzene and some alkylbenzenes in supercritical carbon dioxide, are also found to follow fairly well the proposed correlation, Eq. 10, as liquidlike density is approached. To remove the low fluid density restriction of these models molecular dynamics computations have to be extended beyond $V/V_o = 3$ for solute-to-solvent mass and size ratios other than unity.

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INTRODUCTION

Molecular diffusion data are essential in chemical engineering not only for understanding the fundamentals of transport phenomena but also for practical application in processes involving mass transfer. For all experimental data on diffusion in liquids published over the years, data are not available for diffusion coefficients near the critical temperature. As a consequence, theoretical understanding and empirical correlations derived from available data are probably limited in their scope. In the present work we report experimental values of the tracer diffusion coefficients in cyclohexane (T_c = 553.4 K, P_c = 4.07 MPa) of a number of aromatic hydrocarbons from 298.2 to 523.2 K (T_R = 0.95). The problem with fluid stability, specifically density fluctuations, has prevented precise determination of the diffusion coefficients at 548.2 K (T_R = 0.99).

The experimental results are discussed in terms of diffusion being an activated process. The predictions of a rough-hard-sphere theory (Chandler, 1974; Baleiko and Davis, 1974) are also examined across the widest temperature range ever attempted. The resulting hard-sphere diffusion equation then serves as the basis for developing correlations between tracer diffusivity and solvent molar volume, solute and solvent critical volumes, and their molecular weights.

EXPERIMENTAL

The general principle and application of the Taylor dispersion phenomenon for determining molecular diffusivities over an extended range of temperature has been described elsewhere (Chen et al., 1983). In the apparatus constructed for the present study, a Constametric III metering pump and a UV absorbance detector (both from Laboratory Data Control)

TABLE 1. TRACER DIFFUSIVITIES OBSERVED AND COMPARED TO THE RHS PREDICTION[a,b]

Temp. K	Cyclohexane Density kg/m³	$10^{10}\sigma_1$ m	Benzene 4.85	Toluene 5.07	p-Xylene 5.21	Mesitylene 5.84	Naphthalene 5.73	Phenanthrene 6.05
298.2	774[d]	D_{expt}	1.836 ± 0.007	1.728 ± 0.007	1.645 ± 0.002	1.400 ± 0.009	1.452 ± 0.005	1.199 ± 0.002
		D_{12}^{E}	4.50	4.07	3.79	3.14	3.19	2.78
		D_{12}^{SHS}/D_{12}^{E}	0.57	0.56	0.56	0.54	0.55	0.54
		$D_{12}^{RHS}/D_{\text{expt}}$[c]	0.98	0.93	0.97	0.85	0.86	0.88
333.2	737[d]		3.18 ± 0.02	2.968 ± 0.006	2.85 ± 0.03	2.40 ± 0.01	2.51 ± 0.02	2.120 ± 0.004
			6.18	5.59	5.22	4.34	4.42	3.84
			0.77	0.78	0.78	0.79	0.80	0.78
			1.05	1.03	0.99	1.00	0.98	1.00
373.2	704[e]		5.43 ± 0.02	4.99 ± 0.02	4.74 ± 0.01	4.06 ± 0.02	4.30 ± 0.01	3.64 ± 0.02
			8.26	7.48	6.99	5.83	5.91	5.17
			0.94	0.95	0.97	1.00	1.04	1.01
			1.00	1.00	1.00	1.00	1.00	1.00
423.2	644[e]		9.02 ± 0.02	8.32 ± 0.05	7.86 ± 0.03	6.84 ± 0.04	7.29 ± 0.04	6.17 ± 0.01
			12.31	11.18	10.45	8.77	8.87	7.78
			1.06	1.08	1.09	1.12	1.12	1.13
			1.01	1.01	1.02	1.01	0.95	1.00
473.4	576[e]		14.3 ± 0.1	13.28 ± 0.06	12.5 ± 0.1	10.85 ± 0.03	11.5 ± 0.1	9.81 ± 0.08
			18.27	16.61	15.55	13.10	13.25	11.64
			1.10	1.12	1.14	1.18	1.18	1.18
			0.98	0.98	1.00	1.00	0.96	0.98
523.2	480[e]		24.1 ± 0.3	22.2 ± 0.2	20.5 ± 0.1	18.8 ± 0.2	19.3 ± 0.2	16.3 ± 0.1
			29.23	26.71	25.03	21.19	21.42	18.86
			1.18	1.21	1.29	1.29	1.29	1.27
			1.00	1.02	1.04	1.03	1.00	1.03
523.2	495[e]		22.67 ± 0.04	20.8 ± 0.2	19.5 ± 0.1	17.4 ± 0.1	18.15 ± 0.04	15.26 ± 0.05
			27.78	25.31	23.71	20.04	20.26	17.83
			1.17	1.20	1.22	1.27	1.28	1.25
			1.00	1.02	1.04	1.03	1.00	1.03
523.2	505[e]		22.14 ± 0.06	20.46 ± 0.08	18.8 ± 0.2	16.87 ± 0.09	17.71 ± 0.07	15.0 ± 0.1
			26.75	24.36	22.82	19.32	19.53	17.19
			1.16	1.19	1.22	1.27	1.27	1.25
			0.98	0.99	1.03	1.01	0.98	1.00

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[a] $10^{10}\sigma_2(\text{m}) = 6.14 - 2.00 \times 10^{-3}T(\text{K})$, Chen et al. (1981); values of σ_1's fitted from D_{expt}'s at 373.2 K, the trend in σ_2's parallens that in V_{C1}'s.

[b] All D's expressed in 10^9 m²/s.

[c] $D_{12}^{RHS} = h(D_{12}^{SHS}/D_{12}^{E})D_{12}^{E}$, h = 0.70; for application of the RHS theory see Chen et al. (1981).

[d] Data from Raznjevic (1976).

[e] Data estimated from generalized equation of state of Khan, et al. (1983); prediction verified to within ±1% of experimental data at elevated temperatures and pressures of Reamer and Sage (1957).

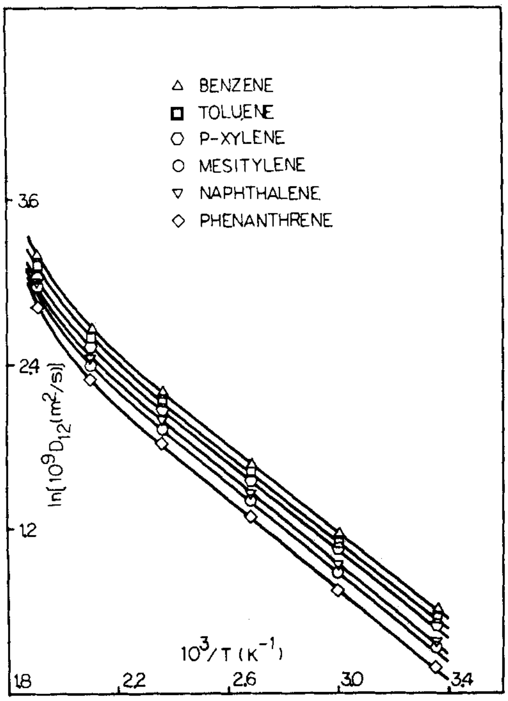

Figure 1. Arrhenius plot of tracer diffusion of aromatic hydrocarbons in liquid cyclohexane.

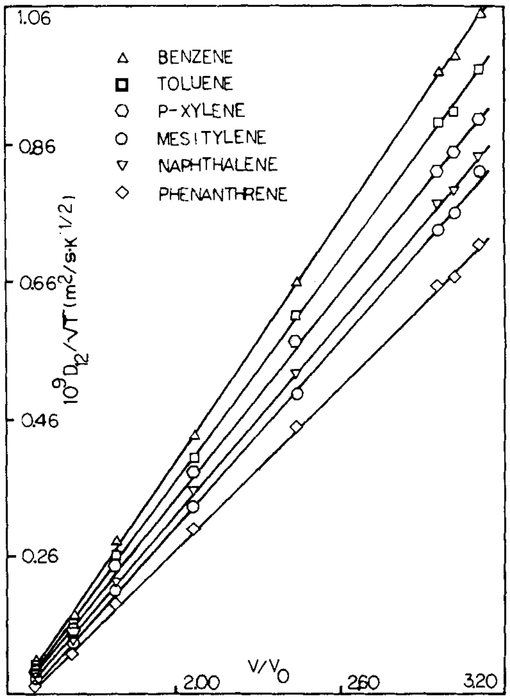

Figure 2. $D_{12}/\sqrt{T}$ vs. V/V_0 for tracer diffusion of aromatic hydrocarbon in liquid cyclohexane.

are used. The temperature of the oil bath is always controlled to within ±0.1 K. The constricted passage prior to the detector is maintained at constant temperature using a temperature controller (Omega Engineering, Inc.) so as to keep pressure fluctuations to within ±0.5% of the readings on a Bourdon-type Heise gauge. The extinction coefficients (at 254 nm) of the solutes under investigation are high enough for the concentrations of the injected solutions to be no more than 1 wt.%. To keep the fluid flowing in the dispersion column in liquid state, a pressure of about 0.2 MPa above the saturation pressure at the oil bath temperature is consistently applied. The effect of the applied pressure on measured diffusivities is found to be negligible from cyclohexane density data except at 523 K, where diffusivities have been measured at three pressures. Each reported diffusivitiy is the mean of at least three measurements, and the standard deviation is normally ±1%.

The solvent cyclohexane (99%+) and solutes benzene (99%+), toluene (99%+), *p*-xylene (99%+), mesitylene (i.e. 1,3,5-trimethylbenzene, 99%), naphthalene (99%+), and phenanthrene (98%+) were all used as received from Aldrich Chemical Co.

RESULTS AND DISCUSSION

Summarized in Table 1 are the tracer diffusivities in liquid cyclohexane of benzene, toluene, *p*-xylene, mesitylene, naphthalene, and phenanthrene as a function of temperature (and density at 523.2 K). The density of cyclohexane solvent is either determined experimentally (Raznjevic, 1976) or estimated with a generalized equation of state recently presented by Khan et al. (1983). It is found that the prediction with this equation agrees with observed values to within ±1% at temperatures up to 510.9 K and pressures up to 3.44 MPa, where experimental data are available (Reamer and Sage, 1957). At temperatures up to 473.4 K, the effect of applying pressures up to 1.79 MPa is found to be negligible, for the density is within 1% of that at the saturation pressure. This allows us to view the tracer diffusivities measured up to 473.4 K as those at vapor-liquid coexistence curve. At 523.2 K we have extrapolated the observed diffusivities at three densities to obtain those corresponding to saturation density: benzene, 24.7; toluene, 22.7; *p*-xylene, 20.9; mesitylene, 19.4; naphthalene, 19.7; phenanthrene, 16.7; all in 10^{-9} m²/s. With all the diffusivities in liquid essentially along the vapor-liquid coexistence curve, we have plotted $\ln D_{12}$ vs. $1/T$ in Figure 1. It is clear that there are positive deviations from the linear relationship as T_R approaches 0.95 for all six solutes. Similar behavior has been observed by Panchenkov et al. (1969) for the self-diffusion of liquid normal alkanes up to their respective critical temperatures. For tracer diffusion data reported here the following equation is found to reproduce the observed values to well within ±1%:

$$\ln(10^9 D_{12}) = -\frac{\alpha}{T} + \beta + \gamma T \tag{1}$$

in which D_{12} is expressed in 10^9 m²/s.

The values of three parameters from best fit are given in Table 2. Although the Arrhenius-type equation, i.e. $\gamma = 0$ in Eq. 1, has been found to be quite versatile in correlating diffusion data, the peculiar behavior of the liquid close to its critical temperature has apparently limited its applicability. However, this observation indicates a need for better understanding the fluid behavior around the critical point. With this note we proceed in what follows to test

TABLE 2. PARAMETER VALUES FOR EQ. 1

	α K	β	$10^5\gamma$ K^{-1}
Benzene	929	2.15	534
Toluene	866	1.78	567
p-Xylene	932	2.13	509
Mesitylene	791	1.12	634
Naphthalene	965	2.08	518
Phenanthrene	1,024	2.27	479

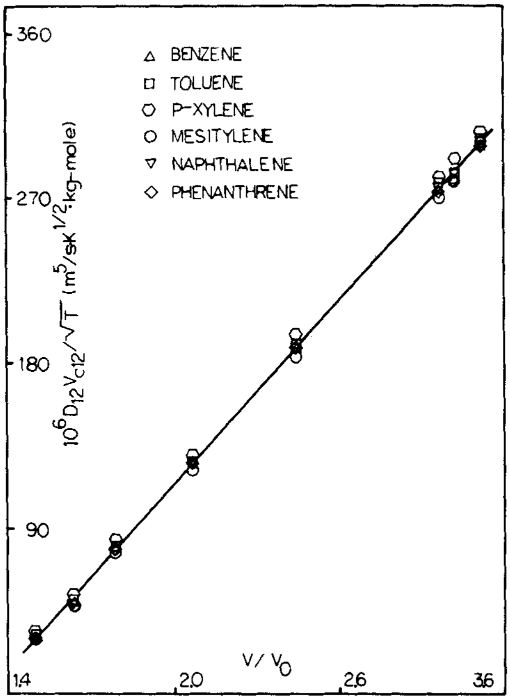

Figure 3. $D_{12}V_{C12}/\sqrt{T}$ **vs.** V/V_o **for tracer diffusion of aromatic hydrocarbons in liquid cyclohexane.**

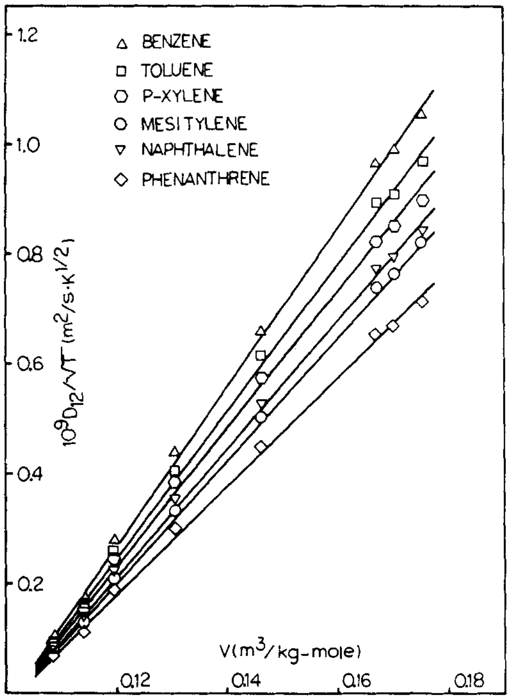

Figure 4. $D_{12}/\sqrt{T}$ **vs.** V **for tracer diffusion of aromatic hydrocarbons in liquid cyclohexane.**

the performance of a rough-hard-sphere (RHS) theory of molecular diffusion.

In the context of the RHS theory, (Chandler, 1974; Baleiko and Davis, 1974), polyatomic molecules of real fluids are modeled as rough hard spheres which undergo binary but dynamically correlated collisions. The molecular roughness arises from the coupling between translational and rotational motion. Crude as the model is, it has been widely accepted as the basis for interpreting diffusion data in real fluids (Bertucci and Flygare, 1975; Jonas and Parkhurst, 1977; Evans et al., 1981; Chen, 1983) because of the availability of computer simulation results for hard-sphere systems (Chen et al., 1981). The RHS model has also been shown to be quite versatile in rationalizing the molecular diffusion in a number of liquids as a function of temperature (Chen et al., 1981). Nonetheless, the present data should permit one to test the theory across the widest temperature range ever attempted. The equations and procedures are as summarized elsewhere (Chen et al., 1983) and will not be repeated here. The effective solvent diameter as a function of temperature was fitted from self-diffusion data (Chen et al., 1981):

$$10^{10}\sigma_2(\mathrm{ml}) = 6.14 - 2.00 \times 10^{-3}T(\mathrm{K}) \tag{2}$$

The effective solute diameter is treated as a parameter, which is fitted from the observed tracer diffusivity at 373.2 K, for its temperature coefficient on the order of 10^{-3} K^{-1} has little effect on the RHS prediction of the tracer diffusivity. The theoretical prediction is compared to experimental results in Table 1, which indicates uniform agreement up to 523.2 K. We remark in passing that the trend in σ_1's follows that in V_{C1}'s. However, the application of the theory for predictive purposes is made difficult by the fact that parameter values have to be back-calculated from experimental data. It will be shown below that the RHS theory in fact implies a useful scheme for correlating diffusion data without involving σ_1.

On the basis of computer simulation on hard-sphere fluids, Dymond (1974) arrived at the following expression for correlating self-diffusion data:

$$D_{11} \propto \left(\frac{T}{M}\right)^{1/2} V_o^{1/3}\left(\frac{V}{V_o} - 1.384\right) \tag{3}$$

in which V_o is the hard sphere close-packed molar volume, and hence

$$\frac{V}{V_o} = \frac{\sqrt{2}}{n_2\sigma_2^3} \tag{4}$$

For tracer diffusion Eq. 3 is rewritten as

$$\frac{D_{12}}{\sqrt{T}} \propto \left(\frac{V}{V_o} - I\right) \tag{5}$$

In Figure 2 $D_{12}/\sqrt{T}$ is plotted against V/V_o for the six solutes studied here. Note that σ_2 found from Eq. 2 is used in Eq. 4 to obtain V/V_o. It is clearly demonstrated that the linear relationship covers the whole temperature range 298.2–523.2 K. Furthermore, the slope of the straight line decreases with increasing solute size. If Eq. 3 were to be extended to tracer diffusion one might want to rationalize the variation in slope with the solute/solvent reduced mass. It turns out that the trend in slope parallels that of the solute critical volume, which is a standard measure of molecular volume, rather than its molecular weight. In particular, the mesitylene molecule is lighter but bulkier than naphthalene. Thus, if one is to collapse the six straight lines in Figure 2 down to a single line, one probably would like to scale the quantity $D_{12}/\sqrt{T}$ with some measure of molecular volume. As shown in Figure 3 a single linear relationship

$$\frac{D_{12}V_{C12}}{\sqrt{T}} = 167.3\left(\frac{V}{V_o} - 1.322\right) \tag{6}$$

is capable of representing quite well all the diffusion data reported in the present work. The absolute average error of prediction using Eq. 6 is 4% and the maximum error is 10%. In Eq. 6 V_{C12} is defined as

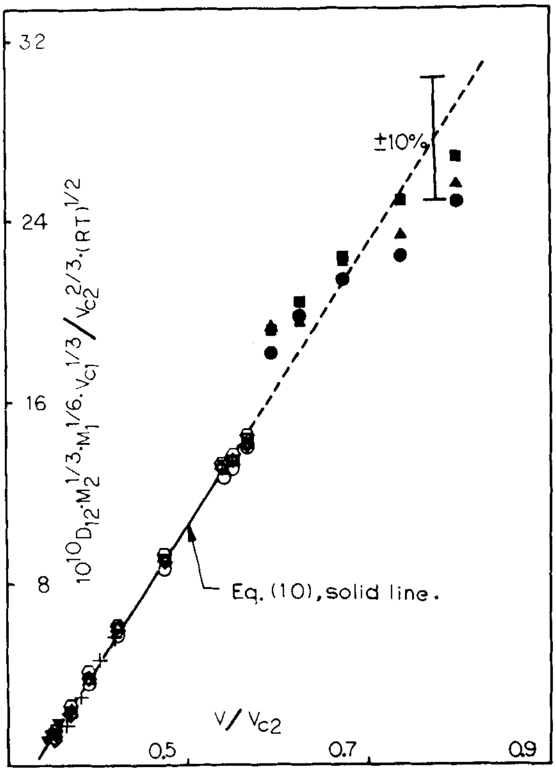

Figure 5. $D_{12}M_2^{1/3}M_1^{1/6}V_{C1}^{1/3}/V_{C2}^{2/3}(RT)^{1/2}$ **vs.** V/V_{C2}**.**

In cyclohexane**, 298.2–523.2 K**

△ benzene **○ mesitylene**
□ toluene **▽ naphthalene**
○ *p*-xylene **◇ phenanthrene**

In cyclohexane**, 298.2–415.9 K**

+ carbon tetrachloride (Chen et al., 1981)

In carbon tetrachloride**, 298.2–313.2 K**

▼ benzene (Caldwell & Babb, 1956)

In supercritical carbon dioxide**, 308.2–328.2 K, 9.5–16.0 MPa (Swaid & Schneider, 1979).**

▲ benzene **● mesitylene**
■ *n*-propylbenzene

$$V_{C12} = \frac{1}{8}(V_{C1}^{1/3} + V_{C2}^{1/3})^3 \qquad (7)$$

in which experimental critical volumes are used where they are available: 0.308 m³/kg·mol, cyclohexane; 0.259, benzene; 0.316, toluene; 0.379, *p*-xylene; 0.433, mesitylene; 0.410, naphthalene (Reid et al. 1977). For phenanthrene it is estimated to be 0.554 m³/kg·mol using Lydersen's group contribution method (Reid et al., 1977), which is found to be good to within ±1% for the other five solutes. The Wilke-Chang (1955) equation along with the viscosity data on cyclohexane up to its T_C (Khalilov, 1962) is found to result in an absolute average deviation of 17% and a maximum error of 40% at 523.2 K.

From comparing the performance of $D_{12}/\sqrt{T}$ vs. V/V_o (Figure 2) to that of $\ln D_{12}$ vs. $1/T$ (Figure 1), one can conclude that while the Arrhenius-type equation is versatile in the sense that the linear relationship holds even for hydrogen-bonded systems (Chen et al., 1983), where the hard-sphere expression consistently fails, the latter turns out to be satisfactory at temperatures up to the critical point for nonassociated systems. In practical applications the plot in Figure 1 requires three parameters, while that in Figure 2 requires two. Additionally, Eq. 6 can be employed to predict the tracer diffusivities of solutes structurally similar to those studied here.

In the absence of self-diffusion data on the solvent, its effective hard-sphere diameter will not be available for calculating V_o. One then is unable to apply Eq. 5 or 6 for correlative or predictive purposes. As an alternative, $D_{12}/\sqrt{T}$ is plotted against V in Figure 4, from which the following equation results

$$\frac{D_{12}V_{C12}}{\sqrt{T}} = 4.11\,(V - 0.101) \qquad (8)$$

It is found that the prediction with Eq. 8 agrees with observed diffusion coefficients to within ±4% on the average, the maximum deviation being 13%. It is also noted that the molar volume at which the diffusive motion is frozen, i.e., 0.101 m³/kg·mol agrees with those found from fluidity and self-diffusion of liquid cyclohexane in the context of Hildebrand's free-volume model (Chen and Chen, 1984).

Finally, we would like to exploit the success of the RHS theory in developing an additional correlation scheme. According to the RHS theory $D_{12}^{\mathrm{RHS}}(m_2/kT)^{1/2}/\sigma_2$ is a function of V/V_o, m_1/m_2, and σ_1/σ_2. Using computer simulation results for tracer diffusion in hard-sphere fluids, as summarized in Table 1 of Chen et al., (1981) along with a molecular roughness factor of 0.70 (Baleiko and Davis, 1974) and a Minitab computer program for multiple regression, we have established the following relationship (σ_1/σ_2 from 0.5 to 1.6, m_1/m_2 from 0.5 to 4.0, V/V_o from 1.5 to 3):

$$\frac{D_{12}^{\mathrm{RHS}}}{\sigma_2}\sqrt{\frac{m_2}{kT}}\left(\frac{m_1}{m_2}\right)^{0.167}\left(\frac{\sigma_1}{\sigma_2}\right)^{1.00} = 0.1101\left[\frac{V}{V_o} - 1.383\left(\frac{m_1}{m_2}\right)^{-0.0165}\left(\frac{\sigma_1}{\sigma_2}\right)^{0.129}\right] \qquad (9)$$

with a correlation coefficient of 0.999.

To facilitate the application of Eq. 9 we have also adopted $V_{Ci}^{1/3}$ as a measure of σ_i and plotted the experimental diffusivities in Figure 5 as $D_{12}M_2^{1/3}M_1^{1/6}V_{C1}^{1/3}/V_{C2}^{2/3}(RT)^{1/2}$ vs. V/V_{C2}. The emerging linear relationship given below is found to perform comparably to Eq. (8):

$$\frac{D_{12}M_2^{1/3}M_1^{1/6}V_{C1}^{1/3}}{V_{C2}^{2/3}(RT)^{1/2}} = 6.19 \times 10^{-9}\left(\frac{V}{V_{C2}} - 0.328\right) \qquad (10)$$

The single intercept in Eq. 10 is the result of limited ranges of m_1/m_2 (from 0.93 to 2.3) and of σ_1/σ_2 (from 0.88 to 1.2) with the solute/solvent systems studied here. It is also noted that Eq. 9 reduces to Dymond's (1974) hard-sphere self-diffusion equation, although the former is developed on the basis of computer simulation for a finite hard-sphere system (i.e., 108 or 500 particles) and the latter on an infinite number of hard spheres. This suggests that in the development of correlations for real fluids, the finiteness of a hard-sphere system on which molecular dynamics is followed causes no real problem. Furthermore, it is now understood that the argument for scaling $D_{12}/\sqrt{T}$ with V_{C12} (instead of solute-solvent reduced mass) to obtain a generalized correlation, Eq. 8, is supported by the fact that $V_{C12} = (0.0223 \pm 0.0003)\,M_1^{1/6}V_{C1}^{1/3}/V_{C2}^{2/3}$ for the six solutes studied here. It is anticipated that the applicability of Eq. 10 is contingent upon the success of the RHS theory for a particular solute-solvent system; however, it may serve as a basis with sound theoretical foundation for correlating tracer diffusion data. Experimental diffusivities across a wide temperature range are rare, but we have collected a few from the literature to test the performance of Eq. 10, as also shown in Figure 5. Among the tracer diffusivities in supercritical carbon dioxide reported by Swaid and Schneider (1979) it is found that Eq. 10 performs reasonably well as liquidlike density is approached. The failure beyond $V/V_{C2} = 0.8$ is attributable to the fact that V/V_o falls far beyond the range $1.5 \leq V/V_o \leq 3$ for which computer simulation results for model hard-sphere fluids are available. (The value of V/V_o can be calculated from Eq. 4 using the density data and $\sigma_2(T)$ for carbon dioxide given in Chen, 1983.) In order for the RHS theory to provide guidance on diffusivity correlation, molecular dynamics computation has to be extended to the less-dense region for solute-to-solvent mass and size ratios other than unity.

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NOTATION

D = molecular diffusivity, m^2/s
h = roughness factor, dimensionless
I = intercept in Eq. 5, dimensionless
k = Boltzmann's constant, 5.776×10^{-16} J/K
M = molecular weight, kg/kg·mol
m = molecular mass, kg
n = number density, m^{-3}
P = pressure, Pa
R = ideal gas constant, 8.314×10^3 J/kg·mol·K
T = temperature, K
V = molar volume, m^3/kg·mol
V_o = hard sphere close-packed volume

Greek Letters

$\left.\begin{matrix}\alpha\\ \beta\\ \gamma\end{matrix}\right\}$ = parameters in Eq. 1
σ = effective hard-sphere diameter, m

Subscripts

1 = solute
2 = solvent
11 = self-diffusion
12 = tracer diffusion
C = critical property
R = reduced property

Superscripts

E = Enskog's theoretical prediction
SHS = smooth-hard-sphere value
RHS = rough-hard-sphere value

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