Tracer Diffusion in Dense Ethanol: A Generalized Correlation for Nonpolar and Hydrogen-Bonded Solvents

Tracer diffusion coefficients were measured for benzene, toluene, mesitylene, naphthalene, and phenanthrene in dense ethanol at $0.56 \leq T_R \leq 1.07$ and $\rho_R \geq 1.44$. The results were used to examine the temperature dependence of the degree of association between ethanol molecules across the entire range of temperature. The hard-sphere tracer diffusion equation and the Stokes-Einstein equation were used to develop two engineering correlations. The former approach was found to be adequate for solvents of relatively compact molecules, and the latter to be more general in its applications. The absolute deviation of prediction from observed values of tracer diffusivities is 4%, with a maximum error of 13%.

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SCOPE

Diffusion coefficients are required for the design of separation processes involving interface mass transfer. The Taylor-Aris dispersion phenomenon was used in the present work to measure the tracer diffusion coefficients of benzene, toluene, mesitylene, naphthalene, and phenanthrene in dense ethanol ($T_c = 516.2$ K; $\rho_c = 275.9$ kg/m^3) from 313.2 to 554.0 K. This was done particularly to meet the need for diffusion data for designing supercritical separation processes. The measured values of tracer diffusivity were employed first to investigate the degree of solvent molecular association as a function of temperature and then to develop an engineering correlation. An alternative correlation scheme was established by empirically modifying the Stokes-Einstein equation. In both correlations, the supercritical dense gases were treated essentially as expanded liquids.

CONCLUSIONS AND SIGNIFICANCE

Using the measured values of the tracer diffusivity of a series of aromatic hydrocarbons (benzene, toluene, mesitylene, naphthalene, and phenanthrene) in both liquid and supercritical dense ethanol at $0.56 \leq T_R \leq 1.07$ and $\rho_R \geq 1.44$, we managed to gather information on the temperature dependence of solvent molecular association. The association number was found to decrease linearly from 2.82 at 293.2 K to 1.85 at 554.0 K. Based on the hard-sphere tracer diffusion equation, a generalized correlation was developed by including the temperature-dependent solvent molecular association. The correlation was found to be adequate for solvents of relatively compact molecules. Alternatively, by empirically modifying the Stokes-Einstein equation we established the other correlation, which turned out to be more general in its applications. Both correlations predict tracer diffusivities that deviate from experimentally determined values to within ± 4% on the average, with a maximum error of 13%. In essence, the present work has provided a basis for correlating data for tracer diffusion in liquids and supercritical dense gases within a consistent framework. In other words, the supercritical dense gases can be treated as expanded liquids as far as molecular association and diffusion are concerned.

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Introduction

Because of its uniqueness in enhanced solubility, preferential extraction of the desired component, and facile precipitation of extractive(s), extraction with supercritical dense fluids has gained great popularity in the energy, food, and pharmaceutical industries in recent years. Of particular interest to the development of such separation processes are equilibrium and transport data over wide temperature and pressure ranges. Although there have been intensive activities in gathering phase equilibrium data (Paulaitis et al., 1983; Franck and Schneider, 1984) there exist relatively few data on transport properties, especially the binary diffusion coefficients. Diffusion coefficients are important not only for understanding transport processes in dense fluids, but also for predicting the rate of interface mass transfer involved in extraction processes.

In a recent series of papers (Sun and Chen, 1984, 1985ab) we have successfully employed the Taylor-Aris dispersion method to determine the tracer diffusivities of a series of aromatic hydrocarbons in dense cyclohexane, *n*-hexane, and 2,3-dimethylbutane up to and beyond solvent critical temperatures. The results have furnished further understanding of diffusion processes in tems of a molecular theory that incorporates Sung and Stell's (1984) formulation of collective molecular motion. Furthermore, correlations have also been developed on the basis of the hard-sphere theory of molecular diffusion (Chandler, 1974) or the corresponding-states principle for self-diffusion (Helfand and Rice, 1960). However, in all these studies both solute and solvent molecules are nonpolar and somewhat compact.

In the present work, we chose to work with ethanol ($T_c = 516.2$ K, $\rho_c = 275.9$ kg/m^3), for which there exists intermolecular hydrogen bonding that normally denies standard theoretical interpretation such as hard-sphere treatment. The Taylor-Aris dispersion technique was used here to measure the tracer diffusivities of benzene, toluene, mesitylene, naphthalene, and phenanthrene in liquid ethanol close to the vapor-liquid coexistence curve over the temperature range covered by $0.61 \leq T_R \leq 0.97$ and in supercritical dense ethanol at $1.00 \leq T_R \leq 1.07$ and $1.44 \leq \rho_R \leq 2.05$. The observed values of tracer diffusion coefficients were used to examine the extent of hydrogen bonding between solvent molecules in the context of a hard-sphere formalism formerly proposed (Sun and Chen, 1984). It appears that both tracer diffusion and viscosity can be treated within the same framework of intermolecular hydrogen bonding across an extremely wide temperature range, $0.56 \leq T_R \leq 1.07$. In addition, based on an empirical correction to the hydrodynamic theory (i.e., the Stokes-Einstein equation), an engineering correlation was generated that covers the entire temperature and density ranges for the present diffusion measurements.

Experimental

The experimental apparatus and procedures are as described previously for subcritical (Sun and Chen, 1984) and supercritical (Sun and Chen, 1985a) diffusion measurements. The solvent ethanol (99%, University of Rochester Medical Center) and solutes benzene (99%+), toluene (99%+), mesitylene (i.e., 1,3,5-trimethylbenzene, 99%), naphthalene (99%+), and phenanthrene (98%+), all from Aldrich Chemical Co., were used as received without further purification except for filtration of the solvent and extremely dilute solutions (typically 0.5 wt.%) through 0.5 μm Teflon membrane (Millipore).

Results and Discussion

Summarized in Table 1 are the observed values of the tracer diffusion coefficients of aromatic hydrocarbon solutes in dense ($\rho_R \geq 1.44$) ethanol as a function of temperature and of ethanol density. Each reported value is the mean of three measurements, and the standard deviation is generally ± 1% of the mean.

Temperature dependence of the degree of association between ethanol molecules

It is well known that ethanol molecules tend to associate with each other via hydrogen bonding. The degree of such association has been studied both by molecular modeling (Smith and Nezbeda, 1984) or direct experimental observation (Narten and Habenschuss, 1984). Alternatively, the molecular association has been incorporated in transport processes and treated as a model parameter, the value of which is then extracted from measured values of binary diffusivities (McKeigue and Gulari, 1984; Kato et al., 1980). In the present treatment of tracer diffusion data in ethanol, we started with the association number of 2.82 for ethanol determined by the x-ray diffraction method at 293.2 K (Narten and Habenschuss, 1984). To investigate the temperature dependence of the association number $\beta(T)$ for associated solvent molecules, let us define

$$D_R \equiv \frac{D_{12}M^{1/6}(\beta M_2)^{1/3}{V_{C1}}^{1/3}}{(\beta V_D^o)^{2/3}(RT_{c2})^{1/2}} \tag{1}$$

$$V_R \equiv \frac{V}{\beta V_D^o} \tag{2}$$

Table 1. Tracer Diffusivities ($10^9 D_{12}$, m^2/s) of Aromatic Hydrocarbon Solutes in Ethanol

	Temperature, K															
	313.2	373.2	423.6	473.4	500.3	516.2	516.2	530.2	530.2	530.2	542.8	542.8	542.8	554.0	554.0	554.0
ρ_2, kg/m^3[a]	772	716	649	557	467	567	469	418	476	544	411	449	517	398	433	491
$10^4\mu_2$, N · s/m^2[b]	8.25	3.25	1.66	0.946	0.593	0.790	0.573	0.494	0.586	0.736	0.465	0.535	0.655	0.458	0.513	0.594
Benzene	2.28	5.60	10.1	18.0	26.8	22.1	29.2	33.0	28.6	23.0	35.4	31.1	26.6	36.6	33.9	29.3
Toluene	2.12	5.11	9.50	16.8	24.5	21.1	26.5	30.4	26.7	21.8	32.2	29.0	24.4	33.3	30.7	27.0
Mesitylene	1.69	4.27	7.79	13.3	20.6	16.7	22.4	26.0	22.4	18.4	27.5	25.0	20.6	28.5	25.2	22.9
Naphthalene	1.73	4.44	8.17	14.2	21.9	18.2	23.5	26.6	23.3	19.1	28.3	25.8	21.5	29.6	27.1	24.2
Phenanthrene	1.43	3.80	7.01	12.1	18.3	15.7	19.9	23.3	20.3	16.6	24.6	22.0	18.8	25.3	24.0	20.8

[a] Densities of liquid ethanol (up to 516.2 K) from Young, S., *Proc. Roy. Soc. Dublin*, **12**, 374 (1910). Densities beyond 516.2 K estimated using Bhattacharyya and Thodos' generalized plot, *J. Chem. Eng. Data*, *9*, 530 (1964).

[b] Viscosities of ethanol from Stephan, K., and K. Lucas, *Viscosity of Dense Fluids*, Plenum Pr., New York (1979).

and

$$T_R \equiv \frac{T}{T_{c2}} \tag{3}$$

where V_D°, the molar volume of a nonassociated solvent at which tracer diffusivities vanish, is adopted as a measure of the solvent molecular size to be consistent with the free-volume treatment of molecular diffusion (Hildebrand, 1977; Dymond, 1974).

For nonassociated solvent, $\beta = 1$, and D_R as defined by Eq. 1 emerges from dimensional analysis with the aid of computer simulation of model hard-sphere fluids for binary tracer diffusion (Sun and Chen, 1984). Using the data for tracer diffusion in liquid cyclohexane from 298.2 to 523.2 K (Sun and Chen, 1984), we arrived at the following equation with $V_D^\circ = 0.105 \pm 0.001$ m³/kmol:

$$\frac{D_R}{T_R^{1/2}} = 4.27 \times 10^{-9}(V_R - 1) \tag{4}$$

The failure of Eqs. 1–4 with $\beta = 1$ to represent tracer diffusion data for benzene in ethanol can be attributed to the temperature-dependent molecular association. However, the same set of equations will be used in the following to extract the value of β as a function of T from the diffusion coefficients reported in Table 1.

In the present treatment of solvent ethanol, we adopted the idea of moving units (Kato et al., 1980; Chen and Chen, 1984). Specifically, to an inert solute molecule both size and mass of a moving unit in the sea of the associated solvent were considered to be augmented by a factor β of a solvent molecule, see Eqs. 1 and 2. In terms of Eq. 4 the tracer diffusivity vanishes at the solvent molar volume βV_D°. Using $\beta = 2.82$ at 293.2 K found by Narten and Habenschuss (1984) and the tracer diffusivities for five aromatic hydrocarbon solutes extrapolated to 293.2 K using the Arrhenius type relationship, we found that for solvent ethanol $V_D^\circ = 0.0188 \pm 0.001$ m³/kmol from the best fit of experimental data to Eq. 4. The effective radius of an ethanol molecule calculated from the fitted value of V_D° turns out to be 1.96×10^{-10} m, a value fairly close to 2.05×10^{-10} m found by Khimenko et al. (1973) in their study of the polarizability and molecular radius of a series of aliphatic alcohols. Equation 4 is then rearranged as follows:

$$\frac{D_{12} M_1^{1/6} M_2^{1/3} V_{c1}^{1/3}}{(4.27 \times 10^{-9})(V_D^\circ)^{2/3}(RT)^{1/2}} = \frac{V}{V_D^\circ}\beta^{-2/3} - \beta^{1/3} \tag{5}$$

which is used to find the value of β as a function of temperature from the observed values of tracer diffusivities in ethanol reported in Table 1. From the plot of β vs. T in Figure 1 the following linear relationship results:

$$\beta(T) = 3.97 - 3.92 \times 10^{-3} T \tag{6}$$

The correction for solvent molecular association is shown in Figure 2 to lead to a generalized linear relationship for the tracer diffusion of benzene in cyclohexane and ethanol across the entire range of V_R and in n-hexane at $V_R \leq 2.0$. It seems likely that the noncompact nature of n-hexane molecules has caused negative deviations for $V_R > 2.0$.

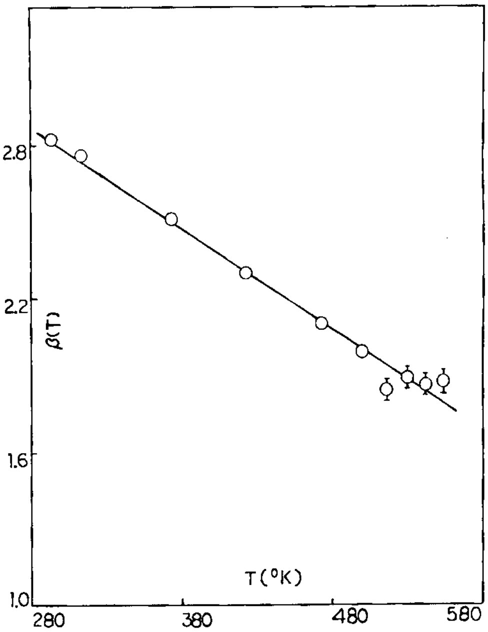

Figure 1. Temperature dependence of association number, $\beta(T)$, in ethanol from 293.2 to 554.0 K.

It is of interest to verify if the value of β predicted from Eq. 6 can be extended for the treatment of shear viscosity. Following Dymond's (1974) fluidity equation based on computer simulation for hard-sphere fluids, and using the viscosity data for cyclohexane from 298.2 to 523.2 K (Khalilov, 1962) and for ethanol from 293.2 to 554.0 K (Stephan and Lucas, 1979), we arrived at the following equation:

$$\frac{T_R^{1/2}}{\mu_R} = 1.67 \times 10^8 (V_R - 1) \tag{7}$$

in which

$$\mu_R \equiv \frac{\mu(\beta V_\mu^\circ)^{2/3}}{(\beta M R T_c)^{1/2}} \tag{8}$$

$$V_R \equiv \frac{V}{\beta V_\mu^\circ} \tag{9}$$

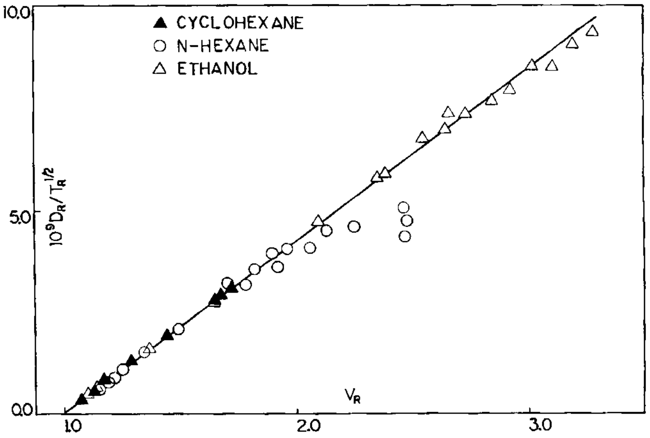

Figure 2. Plot of $D_R/T_R^{1/2}$ vs. V_R.

$\beta = 1$ for tracer diffusion of benzene in cyclohexane at $0.54 \leq T_R \leq 0.95$ and $\rho_R \geq 1.76$; in n-hexane at $0.66 \leq T_R \leq 1.07$ and $\rho_R \geq 1.35$. $\beta(T)$ given by Eq. 6 for tracer diffusion of benzene in ethanol at $0.61 \leq T_R \leq 1.07$ and $\rho_R \geq 1.44$.

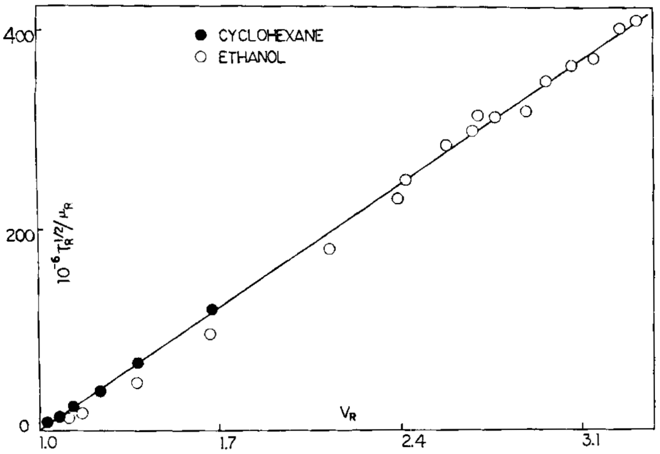

Figure 3. Plot of $T_R^{1/2}/\mu_R$ vs. V_R for viscosity of cyclohexane from 298.2 to 523.2 K, and of ethanol from 293.2 to 554.0 K.

and T_R is as defined by Eq. 3. With $\beta(T)$ predicted with Eq. 6 and $V_\mu^o = V_D^o = 0.0188$ m³/kmol for ethanol and with $\beta = 1$ and $V_\mu^o = V_D^o = 0.105$ m³/kmol for cyclohexane, we plot $T_R^{1/2}/\mu_R$ vs. V_R in Figure 3.

In summary, both viscosity and tracer diffusivity in nonassociated and hydrogen-bonded fluids can be treated in a general framework deduced from hard-sphere equations by allowing the degree of association to vary with temperature. Equation 4 was found to be capable of representing the tracer diffusion coefficients of aromatic hydrocarbons in liquid cyclohexane at $0.54 \leq T_R \leq 0.95$ and $\rho_R \geq 1.76$ (Sun and Chen, 1984), and dense ethanol at $0.61 \leq T_R \leq 1.07$ and $\rho_R \geq 1.44$ (Table 1), with an absolute average deviation of 4% and a maximum deviation of 13%.

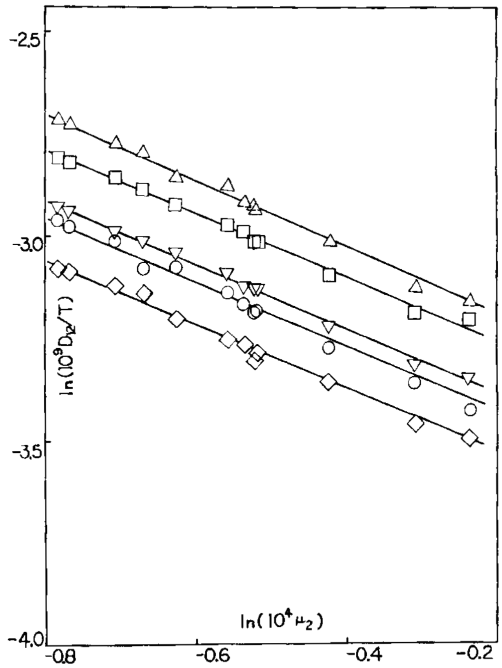

Figure 4. Plot of ln (D_{12}/T) vs. ln (μ_2) for tracer diffusion in ethanol.

△ benzene; □ toluene; ○ mesitylene; ▽ naphthalene; ◇ phenanthrene. T_R = 0.97, 1.00, 1.03, 1.05, 1.07; $\rho_R \geq 1.44$.

While tracer diffusion coefficients in *n*-hexane can be predicted from Eq. 4 with comparable accuracies at $V_R \leq 2.0$, the prediction error may be as high as +30% at $V_R = 2.47$. An alternative correlation scheme is devised in the next section to remove such restrictions.

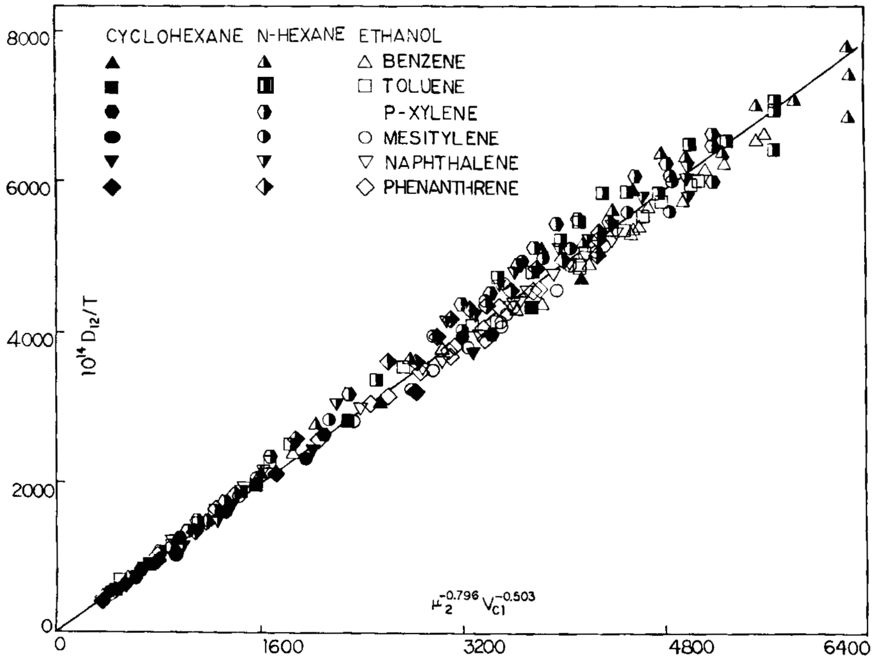

Figure 5. Plot of D_{12}/T vs. $\mu_2^{-0.796}$ $V_{c1}^{-0.503}$ for tracer diffusion coefficients in:

Cyclohexane at $0.54 \leq T_R \leq 0.95$ and $\rho_R \geq 1.76$ *n*-hexane at $0.66 \leq T_R \leq 1.07$ and $\rho_R \geq 1.35$. Ethanol at $0.61 \leq T_R \leq 1.07$ and $\rho_R \geq 1.44$. Solid straight line is represented by Eq. 11.

Development of an engineering correlation by empirically modifying the Stokes-Einstein equation

Traditionally, molecular diffusion has been discussed in terms of the Stokes-Einstein equation. Its failure to correlate diffusion data has become the rule rather than the exception. In a recent paper, Chen and Chen (1984) corrected the Stokes-Einstein equation by considering the solute and solvent molecular size discrepancies from the microfriction point of view (Alwattar et al., 1973). However, their approach was found to be applicable to systems where both solute and solvent molecules are relatively compact. Furthermore, the application was generally limited to temperatures no higher than 373 K. In what follows an alternative modification is tested for the present set of tracer diffusion data in addition to those previously reported (Sun and Chen, 1984, 1985b). In Figure 4 ln (D_{12}/T) is plotted against ln μ_2 for the tracer diffusion of five aromatic hydrocarbon solutes in supercritical dense ethanol. The slopes of the five straight lines are fairly close to each other, -0.798 ± 0.006, which deviates from the Stokes-Einstein value of -1.0. More importantly, it was also noted that the relationship for each solute, namely,

$$\frac{D_{12}}{T} \propto \mu_2^{-0.798} \tag{10}$$

covers the entire temperature and density ranges. Thus, the empirical correction to the Stokes-Einstein equation, Eq. 10, seems to have provided a basis for a consistent treatment of sub- and supercritical diffusion data. Using all the tracer diffusion data given in Table 1 in addition to those in liquid cyclohexane at $0.54 \leq T_R \leq 0.95$ and $\rho_R \geq 1.76$ (Sun and Chen, 1984) and in *n*-hexane at $0.66 \leq T_R \leq 1.07$ and $\rho_R \geq 1.35$ (Sun and Chen, 1985b), we established the following correlation via multiple regression:

$$\frac{D_{12}}{T} = \frac{1.23 \times 10^{-14}}{\mu_2^{0.796} \, V_{c1}^{0.503}} \tag{11}$$

which is plotted in Figure 5. Equation 11 was found to represent experimental data with an absolute deviation of 4% and a maximum error of 13%. The advantage of Eq. 11 over Eq. 4 is that the correlation of Eq. 11 seems to be insensitive to the noncompact nature of *n*-hexane molecules at higher values of V_R, as mentioned for Eq. 4 in the preceding section.

Acknowledgment

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Notation

D = diffusion coefficient, m^2/s
M = molecular weight, kg/kmol
R = ideal gas constant
T = absolute temperature, K
V = molar volume, $m^3/kmol$

Greek letters

β = molecular association number
ρ = density, kg/m^3
μ = viscosity, Ns/m^2

Subscripts

c = critical property
R = reduced property
1 = solute
2 = solvent
12 = tracer diffusion of 1 in 2

Superscript

o = nonassociated solvent

Literature Cited

Alwattar, A. H., M. D. Lumb, and J. B. Birks, "Organic Molecular Photophysics," J. B. Birks, ed., Wiley, New York, **1**, Ch. 8 (1973).

Chandler, D., "Translational and Rotational Diffusion in Liquids. I: Translational Single-Particle Correlation Function," *J. Chem. Phys.*, **60**, 3,500, and "II: Orientational Single-Particle Correlation Function," *J. Chem. Phys.*, **60**, 3,508 (1974).

Chen, H. C., and S. H. Chen, "Diffusion of Crown Ethers in Alcohols," *J. Phys. Chem.*, **88**, 5,118 (1984).

Dymond, J. H., "Corrected Enskog Theory and the Transport Coefficients of Liquids," *J. Chem. Phys.*, **60**, 969 (1974).

Franck, E. U., and G. M. Schneider, "Supercritical Fluid Solvents," *Ber. Bunsenges. Phys. Chem.*, **88**(9) (1984).

Helfand, E., and S. A. Rice, "Principle of Corresponding States for Transport Properties," *J. Chem. Phys.*, **32**, 1,642 (1960).

Hildebrand, J. H., *"Viscosity and Diffusivity,"* Wiley, New York, **1** (1977).

Kato, T., N. Ito, and T. Fujiyama, "Light-Scattering Study of Local Structures in Solutions. Cooperative Translational Motion of Alcohol Molecules in Carbon Tetrachloride Solutions," *Bull. Chem. Soc. Japan*, **53**, 2,167 (1980).

Khalilov, Kh. M., "Viscosity of Isooctane, Cyclohexane, Cyclopentane, and of Their Saturated Vapors," *Zh. Fiz. Khim.*, **36**, 2,474 (1962).

Khimenko, M. T., V. V. Aleksandrov, and N. N. Gritsenko, "The Polarizability and Molecular Radius in Certain Liquids," *Russ. J. Phys. Chem.*, **47**, 1,635 (1973).

McKeigue, K., and E. Gulari, "Light-Scattering Measurements of Diffusion in Binary Solutions Containing an Associating Component," *J. Phys. Chem.*, **88**, 3,472 (1984).

Narten, A. H., and H. Habenschuss, "Hydrogen Bonding in Liquid Methanol and Ethanol Determined by X-Ray Diffraction," *J. Chem. Phys.*, **80**, 3,387 (1984).

Paulaitis, M. E., V. J. Krukonis, and R. T. Kurnik, "Supercritical Fluid Extraction," *Rev. Chem. Eng.*, **1**, 179 (1983).

Smith, W. R., and I. Nezbeda, "A Simple Model for Associated Fluids," *J. Chem. Phys.*, **81**, 3,694 (1984).

Stephan, K., and K. Lucas, *"Viscosity of Dense Fluids,"* Plenum Pr., New York (1979).

Sun, C. K. J., and S. H. Chen, "Tracer Diffusion of Aromatic Hydrocarbons in Liquid Cyclohexane up to Its Critical Temperature," *AIChE J.*, **31**, 1,510 (1985).

———, "Diffusion of Benzene, Toluene, Naphthalene, and Phenanthrene in Supercritical Dense 2,3-Dimethylbutane," *AIChE J.*, **31**, 1,904 (1985).

———, "Binary Diffusion in Dense Fluids up to Supercritical Region," Paper No. 25e, AIChE Natl. Meet., Houston (Mar., 1985).

Sung, W., and G. Stell, "Theory of Transport in Dilute *Solutions*, Suspensions, and Pure Fluids. I: Translational Diffusion," *J. Chem. Phys.*, **80**, 3,350 (1984).

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