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Application of Rough Hard-Sphere Theory to Diffusion in *n*-Alkanes[1]

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Tracer diffusion coefficients are reported for *n*-alkane solutes in *n*-dodecane, *n*-eicosane, *n*-eicosane, and *n*-octacosane in the temperature range 304–533 K at 1.38 MPa. Rough hard-sphere theory is used to interpret the data. The translational–rotational coupling parameters are determined for each solute–solvent pair at each temperature. The nature of the coupling parameter and the possibility of relating it to molecular properties and temperature in a homologous series are discussed.

KEY WORDS: hard-sphere theory; *n*-alkanes; roughness factor; tracer diffusion.

1. INTRODUCTION

The interpretation of tracer diffusion measurements in polyatomic fluids has for some time been based on an extension of a model developed by Chandler [1] for self-diffusion. In this model, tracer diffusion coefficients in a real fluid are approximated by a rough hard-sphere (RHS) fluid which is related to the smooth hard-sphere fluid by the expression

$$D_{12,\mathrm{RHS}} = A_{12} D_{12,\mathrm{SHS}} \tag{1}$$

where A_{12} is a roughness factor that accounts for the effect of coupling between translational and rotational momentum exchange between the solvent and the solute molecules. A_{12} can take any value between 0 and 1. Normally, $D_{12,\mathrm{SHS}}$ is expressed as a ratio that corrects the Enskog diffusion

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coefficients for the effect of correlated molecular motions at high densities. Therefore, Eq. (1) can be written as

$$D_{12,\mathrm{SHS}} = \left(\frac{D_{12,\mathrm{SHS}}}{D_{12,E}}\right) D_{12,\mathrm{E}} \tag{2}$$

$D_{12,\mathrm{E}}$ is the Enskog expression for tracer diffusion and is given as [2]

$$D_{12,\mathrm{E}} = \frac{3}{8\sigma_{12}^2 n}\left(\frac{kT}{\pi m_{12}}\right)^{1/2} \frac{1}{g(\sigma_{12})} \tag{3}$$

where n is the fluid density, $g(\sigma_{12})$ the contact value of the pair correlation function of hard spheres, k Boltzmann's constant, T the absolute temperature, σ_{12} the mean of σ_1 and σ_2, and m_{12} the reduced mass of the solute (11) and the solvent (2). The contact value of the pair correlation function is given by [3]

$$g(\sigma_{12}) = \frac{1}{1-\eta} + \frac{3\eta\sigma_1}{(1-\eta)^2(\sigma_1+\sigma_2)} + \frac{\eta^2\sigma_1}{2(1-\eta)^3\sigma_2} \tag{4}$$

where $\eta = \pi n \sigma_2^3/6$ for tracer diffusion.

Various investigators have used the theory in the above form to interpret tracer diffusion coefficients in a wide variety of systems [4–6]. However, the difficulties involved in assigning values to the effective hard-sphere diameter and the roughness factor have prevented the development of predictive equations based on the RHS theory. In addition, $D_{12,\mathrm{SHS}}/D_{12,\mathrm{E}}$ values have been extracted by interpolation of limited and inaccurate MD simulation data of Alder et al. [7] which resulted in large uncertainties in the calculations. Recent MD simulation data of Easteal and Woolf [8] at closely spaced mass ratios ($0.10 \leqslant M_1/M_2 \leqslant 1.67$) and size ratios ($0.5 \leqslant \sigma_1/\sigma_2 \leqslant 1.0$) at reduced volumes between 1.5 and 2.0 enables one to determine $D_{12,\mathrm{SHS}}/D_{12,E}$ with an acceptable accuracy.

At present, there is no technique to estimate A_{12} from molecular parameters. The objective of our study is to determine the nature of A_{12} in a homologous series, in binary n-alkane systems. Such a study is required before a predictive equation based on the RHS model can be developed. The results of the study also show the validity of some of the correlations for tracer diffusion based on the assumption that A_{12} equals A for self-diffusion [9, 10].

2. EXPERIMENTAL WORK

The tracer diffusion coefficients of n-alkane solutes ranging from octane to hexadecane are measured in n-alkane solvents from heptane to octacosane using the Taylor dispersion technique. The temperature range was 298–573 K and the pressure was 1.38 MPa. The details of the equipment and the method are given elsewhere [11]. The data are analyzed employing a parameter estimation technique [12] based on the Taylor dispersion concentration profile given by the equation

$$C = \frac{M}{2\pi R^2 \sqrt{\pi K t}} \exp\left(\frac{-(L-\bar{u}t)^2}{4Kt}\right) \tag{5}$$

where

$$K = D_{12} + \frac{R^2 \bar{u}^2}{48 D_{12}} \tag{5a}$$

The method is superior in terms of accuracy to other data analysis techniques in the literature.

3. RESULTS AND DISCUSSION

Values of hard-sphere diameters of both solute and solvent molecules are needed as a function of temperature in order to extract A_{12} values from the model. The $\sigma(T)$ can be determined by fitting self diffusion data to the RHS model [13]. However, high-pressure self-diffusion data are not available for *n*-alkanes used in this work. A different approach is to calculate $\sigma(T)$ from liquid molar volume data along the freezing line using the relationship

$$\sigma(T) \times 10^{-7} = 0.11611(V_m)^{1/3} \tag{6}$$

where σ is in m and V_m is in $m^3 \cdot mol^{-1}$. Equation (6) is based on MD simulation results that show that the smooth hard spheres go through a

Table I. Core Diameters at the Melting Point for *n*-Alkanes

	T_m (K)	$\sigma_m \times 10^{10}$ (m)
C_8H_{18}	216.4	6.165
$C_{10}H_{22}$	243.5	6.623
$C_{12}H_{26}$	263.6	7.045
$C_{14}H_{30}$	279.0	7.380
$C_{16}H_{34}$	291.3	7.705
$C_{20}H_{42}$	309.2	8.288
$C_{28}H_{58}$	334.6	9.234

Table II. Tracer Diffusion in *n*-Dodecane at 304–443 K and at 1.38 MPa

	Solute				
	C_8	C_{10}	C_{12}	C_{14}	C_{16}
304 K					
D_{12}^{exp}	1.27_{02}	1.09_{04}	0.96		
R_{12}	0.68	0.70	0.73		
A_{12}	0.36	0.35	0.34		
373 K					
D_{12}^{exp}	3.33_{02}	2.95_{12}	2.61		
R_{12}	0.87	0.91	0.96		
A_{12}	0.49	0.49	0.48		
443 K					
D_{12}^{exp}	6.79_{12}	5.83_{06}	5.23		
R_{12}	0.99	1.02	1.09		
A_{12}	0.61	0.60	0.58		

Table III. Tracer Diffusion in *n*-Hexadecane at 323–513 K and at 1.38 MPa

	Solute				
	C_8	C_{10}	C_{12}	C_{14}	C_{16}
323 K					
D_{12}^{exp}	1.19_{03}	0.99_{02}	0.95_{09}		0.68
R_{12}	0.64	0.67	0.68		0.72
A_{12}	0.30	0.28	0.30		0.26
371 K					
D_{12}^{exp}	2.31_{02}	2.06_{03}			1.43
R_{12}	0.78	0.80			0.88
A_{12}	0.37	0.37			0.34
443 K					
D_{12}^{exp}	5.19_{08}	4.35_{05}	4.09_{11}		3.23
R_{12}	0.90	0.92	0.95		1.04
A_{12}	0.50	0.48	0.50		0.45
513 K					
D_{12}^{exp}	9.50_{44}		7.08_{21}		5.76
R_{12}	0.98		1.03		1.13
A_{12}	0.61		0.57		0.52

Table IV. Tracer Diffusion in *n*-Eicosane at 375–534 K and at 1.38 MPa

	Solute				
	C_8	C_{10}	C_{12}	C_{14}	C_{16}
375 K					
D_{12}^{exp}	1.85_{06}		1.33_{01}		1.06_{03}
R_{12}	0.70		0.73		0.77
A_{12}	0.31		0.29		0.27
413 K					
D_{12}^{exp}	2.86_{02}	2.43_{01}	2.13_{01}	1.87_{03}	1.68_{02}
R_{12}	0.79	0.82	0.84	0.84	0.86
A_{12}	0.35	0.34	0.34	0.33	0.32
454 K					
D_{12}^{exp}	4.22_{01}		3.19_{01}		2.56_{02}
R_{12}	0.84		0.89		0.93
A_{12}	0.40		0.39		0.37
495 K					
D_{12}^{exp}	6.09_{04}	5.33_{02}	4.65_{03}	4.15_{02}	3.75_{02}
R_{12}	0.90	0.92	0.94	0.97	1.00
A_{12}	0.45	0.45	0.44	0.43	0.41
534 K					
D_{12}^{exp}	8.34_{00}		6.36_{06}		5.08_{26}
R_{12}	0.94		1.02		1.03
A_{12}	0.49		0.47		0.45

Table V. Tracer Diffusion in *n*-Octacosane at 373–534 K and at 1.38 MPa

	Solute				
	C_8	C_{10}	C_{12}	C_{14}	C_{16}
373 K					
D_{12}^{exp}	1.21_{03}		0.89_{00}		0.71_{01}
R_{12}	0.61		0.64		0.69
A_{12}	0.21		0.20		0.18
413 K					
D_{12}^{exp}	2.16_{01}		1.56_{05}		1.25_{01}
R_{12}	0.68		0.73		0.78
A_{12}	0.26		0.25		0.24
454 K					
D_{12}^{exp}	3.20_{09}		2.37_{01}		1.89_{02}
R_{12}	0.75		0.81		0.86
A_{12}	0.30		0.29		0.27
495 K					
D_{12}^{exp}	4.70_{07}		3.59_{04}		2.84_{10}
R_{12}	0.81		0.87		0.90
A_{12}	0.34		0.33		0.31
534 K					
D_{12}^{exp}	6.33_{08}		4.82_{09}		3.91_{04}
R_{12}	0.87		0.91		0.97
A_{12}	0.37		0.36		0.34

fluid–solid transition at a reduced density of $n\sigma^3 = 0.943$ [14]. Finally, the formula presented by Protopapas et al. [15] can be used.

$$\sigma(T) = \sigma_m \frac{(1 - B(T/T_m)^{1/2})}{(1 - B)} \tag{7}$$

In Eq. (7), σ_m is the hard-sphere diameter at the melting temperature T_m and B is a constant related to the curvature of the minimum of the intermolecular potential.

A combination of Eqs. (6) and (7) is used to calculate $\sigma(T)$ of solute and solvent molecules due to lack of high-pressure density data at the temperature range of our diffusion measurements. The hard-sphere diameter at the normal melting point, σ_m, is calculated from the density at the melting point using Eq. (6), and then using this value in Eq. (7), σ at each temperature is determined. The constant B was fixed at 0.069 since this is the

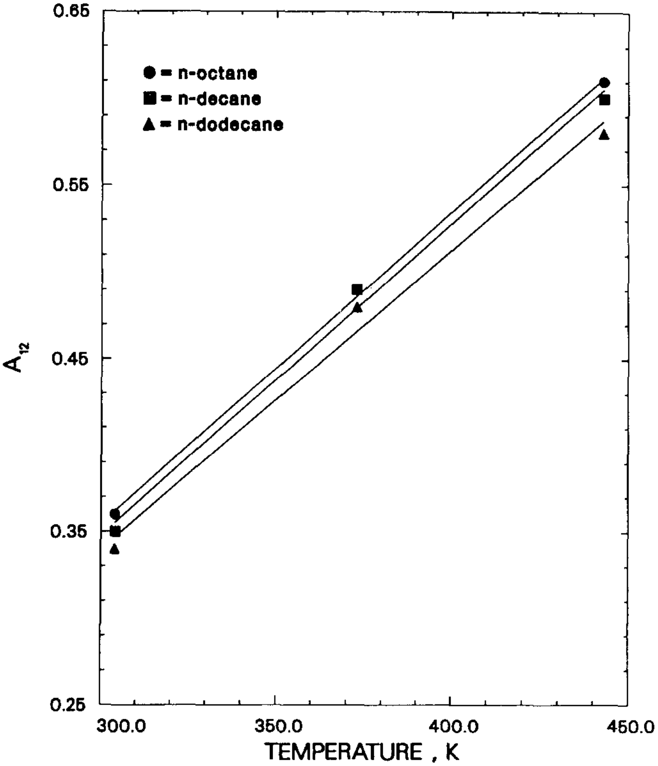

Fig. 1. Roughness factors for tracer diffusion in *n*-dodecane.

value for methane [16] and very close to that for *n*-hexane [17]. In addition, the temperature dependency of characteristic volumes ($V_0 = N\sigma^3/\sqrt{2}$) has been reported to be almost universal among hydrocarbons from ethane to *n*-hexane [18].

The values of σ_m for *n*-alkanes in this work are given in Table I. The values of σ_1 and σ_2 are calculated using Eq. (7) at each measurement temperature. From σ_2 and the density of the solvent, V/V_0 values are calculated. At each reduced volume, $D_{12,\mathrm{SHS}}/D_{12,\mathrm{E}}$ ratios are evaluated by careful graphical interpolation of MD simulation data of Easteal and Woolf [4]. A_{12} values for each solute and solvent pair at each temperature are then back calculated using Eqs. (2) and (4). The results are presented in Tables II–V. In these tables, subscript numbers represent the standard deviation; that is, 1.27_{02} represents a value of $1.27 \pm 0.02 \times 10^{-9}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$, and R_{12} represents $D_{12,\mathrm{SHS}}/D_{12,\mathrm{E}}$.

The self-diffusion coefficients for dodecane and hexadecane are

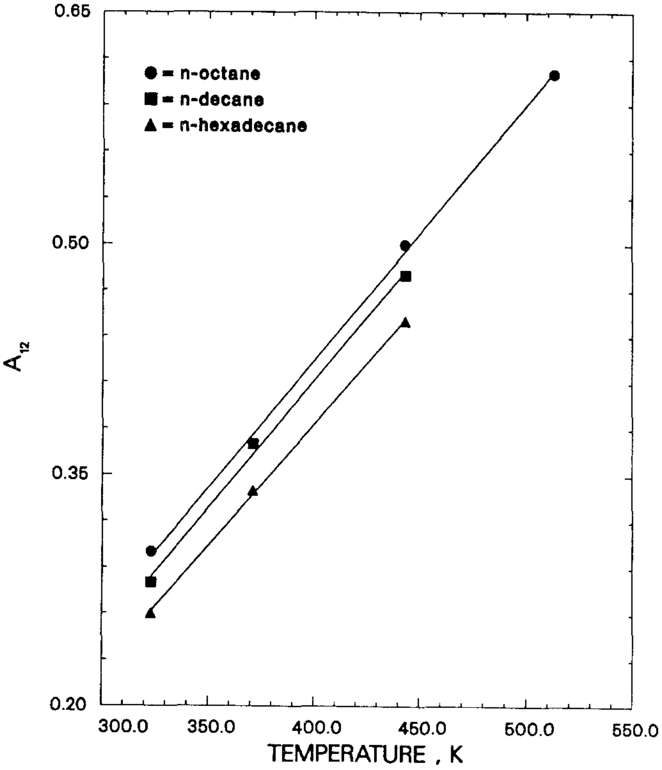

Fig. 2. Roughness factors for tracer diffusion in *n*-hexadecane.

generated using the equations given by Ertl and Dulien [19]. The A values for self-diffusion are back calculated in the same manner using the MD calculations of Easteal et al. [20] for self-diffusion.

We have limited our analysis to the range $1.5 \leqslant V/V_0 \leqslant 2$ and $0.5 \leqslant \sigma_1/\sigma_2 \leqslant 1.0$ in order not to extrapolate the results of MD simulations. However, this approach is valid in any temperature and size-ratio range provided that MD simulation data are available.

A_{12} values calculated from the data are small, which shows that considerable translational and rotational coupling exists between the solute and the solvent molecules in n-alkane systems. A_{12} values are plotted versus temperature for each of the solvents in Figs. 1–4. The lines are determined by a linear least-squares fit for each solute solvent pair. A_{12} shows a marked temperature dependence, which contradicts Chandler's original treatment that the coupling factor should be constant or, at most, a weak function of temperature. In the case of dodecane and hexadecane, A_{12}

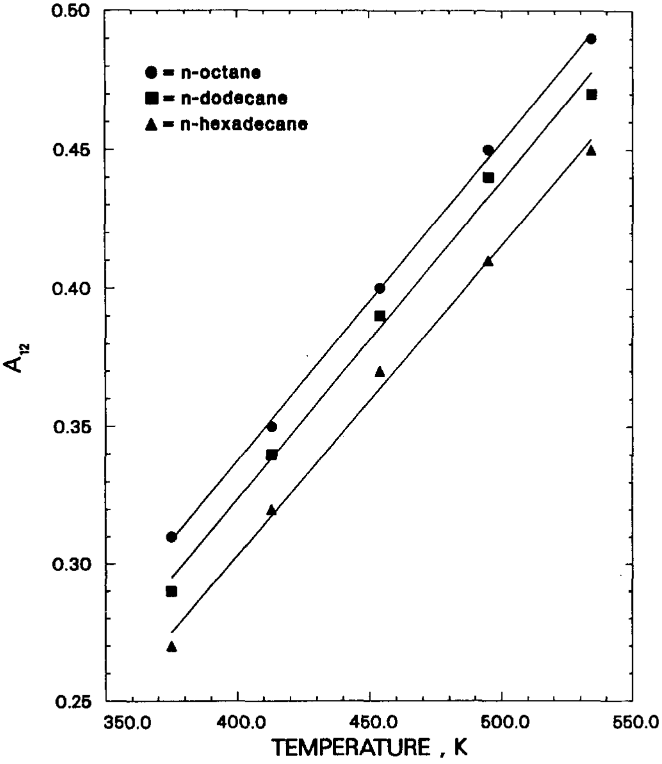

Fig. 3. Roughness factors for tracer diffusion in n-eicosane.

approaches A for self-diffusion as the size and mass of the solute molecule approach those of the solvent molecule. In addition, A_{12} values decrease by an increase in the solvent's molecular mass and size.

Dymond et al. [21] reported a similar approach for tracer diffusion in octamethylcyclotetrasiloxane (OCMTS). A_{12}'s show a similar trend in their analysis except for the solutes methanol and ethanol. The discrepancy is related to the effect of a possible hydrogen bonding between the solute and the solvent. The lack of such a discrepancy in a weakly interacting homologous series shows that their conclusion is probably correct. Self-diffusion A was found to be 0.20 at $V/V_0 = 1.607$ in their analysis by taking σ as 7.775×10^{-10} m. Our values of A_{12} for *n*-eicosane, when extrapolated to self-diffusion, yield an $A = 0.24$ at $V/V_0 = 1.622$. The σ was calculated to be 8.230×10^{-10} m under this condition. The two molecules are similair in mass and size, however, OCMTS has an aglobular structure compared to

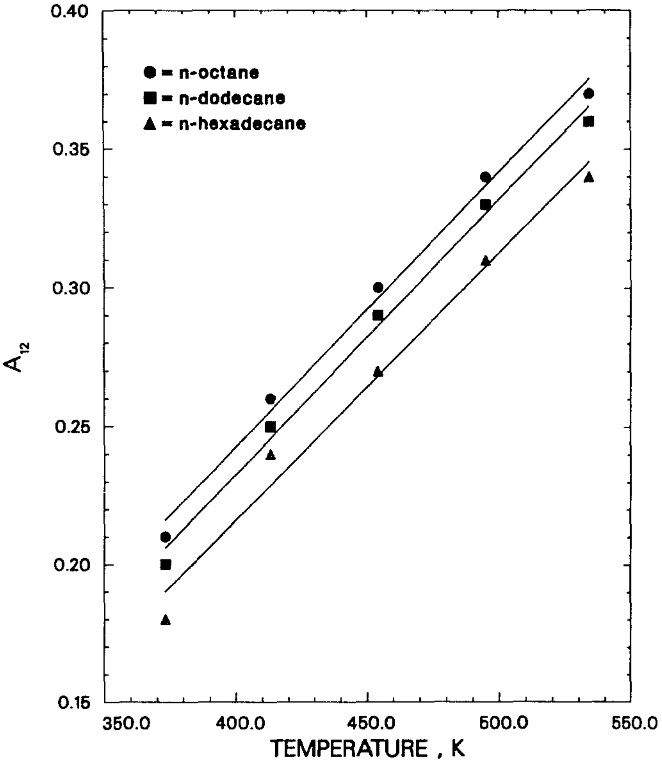

Fig. 4. Roughness factors for tracer diffusion in *n*-octacosane.

the straight long-chain structure of *n*-eicosane. Similar A values imply that A is a stronger function of size and mass of the molecule than the shape.

The parallel nature of the lines in Figs. 1–4 suggests that A_{12} can possibly be related to molecular parameters and temperature. A careful examination of the results shows that A_{12} values increase almost linearly with the decreasing carbon number of the solute. Therefore, by using this approach, it seems highly possible to predict tracer diffusion coefficients accurately with a knowledge of the self-diffusion coefficient for the solvent in binary systems of *n*-alkanes over the entire temperature range. MD simulations for size ratios greater than unity are needed to extend the above analysis to the rest of our data. In addition, a consistent method for determining the hard-sphere diameters is necessary since a slight change in the diameter may make a difference of several percent in the calculated A_{12} values.

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