

Translational Rotational Coupling Parameters for Mutual Diffusion in Normal Alkanes

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Mutual diffusion coefficients in liquids over an extended temperature and pressure range are needed to predict mass-transfer rates. Furthermore, a detailed study of mutual diffusion in liquids is important for our understanding of molecular motions and interactions in such systems. The interpretation of mutual diffusion measurements in dense fluids is based on a model developed by Chandler (1975) for self-diffusion and viscosity coefficients. The mutual diffusion coefficient is given by the expression (Bertucci and Flygare, 1975):

$$D_{12,RHS} = A_{12} \left(\frac{D_{12,SHS}}{D_{12,E}} \right) D_{12,E} \quad \text{where } 0 < A_{12} \leq 1 \quad (1)$$

where $D_{12,E}$ is the Enskog expression given by (Chapman and Cowling, 1939):

$$D_{12,E} = \frac{3}{8n\sigma_{12}^2} \left[\frac{kT}{2\pi} \frac{(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \frac{1}{g(\sigma_{12})} \quad (2)$$

$g(\sigma_{12})$ is the radial distribution function at contact (Carnahan and Starling, 1973)

$$g(\sigma_{12}) = \frac{\sigma_1 g(\sigma_{22}) + \sigma_2 g(\sigma_{11})}{(\sigma_1 + \sigma_2)} \quad (3)$$

and $g(\sigma_{ii})$ is given by:

$$g(\sigma_{ii}) = \frac{1}{1 - \xi} + \frac{3y_i}{2(1 - \xi)^2} + \frac{y_i^2}{2(1 - \xi)^3} \quad (4)$$

where

$$\xi = \sum_i n_i \pi \sigma_i^3 / 6 \quad (5)$$

$$y_i = (\sigma_i \xi_j + \sigma_j \xi_i) / \sigma_j \quad (6)$$

and σ_i is the effective hard sphere diameter and n_i is the number density.

$(D_{12,SHS}/D_{12,E})$ corrects the Enskog diffusion coefficient for the effect of correlated molecular motions at high densities. These effects have been studied quantitatively (Alder et al., 1974; Eastale and Woolf, 1984; Eastale and Woolf, 1988) and the resulting correction factors, $(D_{12,SHS}/D_{12,E})$ ratios, are usually given as a function of m_1/m_2 , σ_1/σ_2 , and V/V_o where V_o is the closed packed hard sphere of the fluid expressed as:

$$V_o = \sum_i N 2^{-1/2} (x_i \sigma_i^3) \quad (7)$$

A_{12} accounts for the effect of coupling between translational and rotational momentum exchange between unlike molecules. The experimental diffusion coefficient is related to the $D_{12,RHS}$ by the expression:

$$D_{12,exp} = D_{12,RHS} \left[1 + \frac{\partial \ln a_1}{\partial \ln x_1} \right] \quad (8)$$

where $(1 + \partial \ln a_1 / \partial \ln x_1)$ accounts for the nonideality of the system and is unity for ideal mixtures.

At present, there is no way to calculate A_{12} and the value can only be extracted from experimental data. The diffusion of a single solute species at very low concentration in a pure molecular fluid is a special case of mutual diffusion defined by the limiting mutual diffusion coefficient. Therefore, we have measured the

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limiting mutual diffusion coefficients of *n*-alkane solutes ranging from methane to *n*-tetradecane in *n*-octane (Erkey and Akgerman, 1989) and in *n*-hexadecane to study the nature of the coupling parameter in a homologous series. The temperature range of the experiments for *n*-hexadecane was 300–541 K. However, the analysis of the data is restricted to the temperature range 421–541 K which corresponds to a reduced volume range of 1.58–1.99. The data for 300–371 K are presented for future development of the liquid-state theories for nonspherical molecules near the melting point and for development of predictive equations.

Results and Discussion

We have used the Taylor dispersion technique to measure the diffusion coefficients. The details of the experimental assembly and procedure are given elsewhere (Matthews and Akgerman, 1987; Rodden, 1988). The temperature dependency of the measured limiting mutual diffusion coefficients of *n*-alkanes in *n*-hexadecane is shown in Figure 1. Each data point is the average of at least three repetitive measurements. The average standard deviation is 0.6% and the accuracy of the data is estimated to be within $\pm 1\%$.

The translational rotational coupling parameter can be extracted from experimental data using the equation:

$$A_{12} = \frac{D_{12,exp}}{\left(1 + \frac{\partial \ln a_1}{\partial \ln x_1} \left(\frac{D_{12,SHS}}{D_{12,E}} \right) \right) D_{12,E}} \quad (9)$$

The procedure for calculation of the effective hard sphere diam-

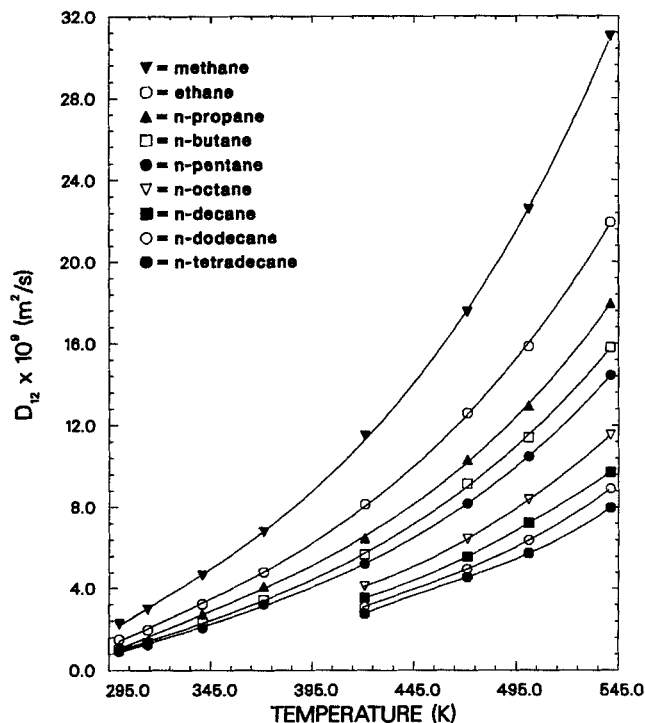


Figure 1. Temperature dependency of limiting mutual diffusion coefficients in *n*-hexadecane at $0.86 \times 10^6 \text{ N/m}^2$.

Table 1. Close-Packed Hard-Sphere Volumes* of *n*-Alkanes and Correction Factors for Each Solute-Solvent Pair for Diffusion in *n*-Hexadecane

		Temperature (K)			
		421	471	501	541
CH ₄	<i>V</i> _o	16.64	16.26	16.06	15.81
	<i>R</i> ₁₂	0.63	0.73	0.78	0.85
C ₂ H ₆	<i>V</i> _o	28.86	28.47	28.25	27.98
	<i>R</i> ₁₂	0.61	0.72	0.76	0.84
C ₃ H ₈	<i>V</i> _o	40.45	39.80	39.44	39.01
	<i>R</i> ₁₂	0.62	0.73	0.78	0.85
C ₄ H ₁₀	<i>V</i> _o	53.27	52.55	52.15	51.66
	<i>R</i> ₁₂	0.63	0.75	0.80	0.87
C ₅ H ₁₂	<i>V</i> _o	62.17	61.54	61.28	61.03
	<i>R</i> ₁₂	0.65	0.77	0.83	0.89
C ₈ H ₁₈	<i>V</i> _o	100.20	98.00	96.80	95.33
	<i>R</i> ₁₂	0.68	0.83	0.88	0.97
C ₁₀ H ₂₂	<i>V</i> _o	128.06	124.60	122.55	119.90
	<i>R</i> ₁₂	0.70	0.85	0.91	1.00
C ₁₂ H ₂₆	<i>V</i> _o	154.40	149.20	146.30	142.50
	<i>R</i> ₁₂	0.73	0.87	0.95	1.02
C ₁₄ H ₃₀	<i>V</i> _o	180.80	175.00	171.60	167.00
	<i>R</i> ₁₂	0.75	0.90	0.98	1.04
C ₁₆ H ₃₄	<i>V</i> _o	207.70	200.90	196.80	191.30
	<i>R</i> ₁₂				

*($10^6 \text{ V}_o, \text{ m}^3/\text{mol}$)

eters for the solute and the solvent molecules at each temperature, and for calculation of the ($D_{12,SHS}/D_{12,E}$) ratios for each solute-solvent pair are given elsewhere (Erkey and Akgerman, 1989). The density of *n*-hexadecane at each temperature was calculated using the correlation given in Orwell and Flory (1967). The *V*_o values for the solutes and the solvent and ($D_{12,SHS}/D_{12,E}$) for each pair are given in Table 1. In this table, *R*₁₂ represents ($D_{12,SHS}/D_{12,E}$).

The translational-rotational coupling parameters, *A*₁₂'s, were then extracted from the experimental data using the *R*₁₂ values from molecular dynamics simulations and the Enskog diffusivity employing Eq. 9, together with Eq. 2–8 (in the case of limiting mutual diffusion, *n*₁ and $\partial \ln a_1 / \partial \ln x_1 = 0$). The results for *n*-hexadecane are presented in Table 2.

Table 2. Translational-Rotational Coupling Parameters for Each Solute-Solvent Pair for Diffusion in *n*-Hexadecane

Solute	Temperature (K)				Average
	421	471	501	541	
CH ₄	0.53	0.52	0.53	0.54	0.53 ± 0.01
C ₂ H ₆	0.62	0.61	0.61	0.62	0.62 ± 0.01
C ₃ H ₈	0.65	0.65	0.64	0.66	0.65 ± 0.01
C ₄ H ₁₀	0.69	0.70	0.68	0.70	0.69 ± 0.01
C ₅ H ₁₂	0.71	0.70	0.70	0.72	0.71 ± 0.01
C ₈ H ₁₈	0.76	0.72	0.74	0.74	0.74 ± 0.02
C ₁₀ H ₂₂	0.76	0.73	0.73	0.71	0.73 ± 0.02
C ₁₂ H ₂₆	0.73	0.72	0.70	0.72	0.72 ± 0.01
C ₁₄ H ₃₀	0.72	0.71	0.69	0.71	0.71 ± 0.01

The translational-rotational coupling parameter seems to be independent of temperature for each solute solvent pair. Furthermore, the parameter can be considered as constant for solutes ranging from butane to tetradecane. The calculated values deviate around a mean value of 0.72. As the solute molecules become smaller and lighter than butane, the amount of translational rotational coupling starts to increase. We have previously reported diffusion measurements for *n*-alkane solutes in *n*-octane in the reduced volume range, 1.53–1.99 (Erkey and Akgerman, 1989). The values of the coupling parameter deviate around a mean value of 0.90 for solutes ranging from propane to tetradecane diffusing in *n*-octane. The lower value of A_{12} for diffusion in *n*-hexadecane suggests that the amount of translational-rotational coupling increases with the increasing carbon number of the solvent molecule. Based on these findings, the same analysis has been performed for diffusion measurements of *n*-alkane solutes ranging from *n*-octane to *n*-hexadecane in *n*-eicosane (Rodden et al., 1988). The values of the coupling parameter fluctuate around a mean value of 0.61 for these *n*-alkane solutes in *n*-eicosane in the temperature range, 413–534 K.

Figure 2 shows a plot of A_{12} as a function of carbon number of the solvent molecule. The linear variation of the parameter with the carbon number of the solvent molecule enables one to estimate the A_{12} values for other *n*-alkane solvents using the equation:

$$A_{12} = -0.024C + 1.094 \quad (10)$$

where C is the carbon number of the solvent molecule. Figure 3 gives a plot of calculated versus predicted diffusivities using Eq. 10, together with Eqs. 1–8, for the systems employed. The data cover solutes from propane to tetradecane in *n*-octane, butane to

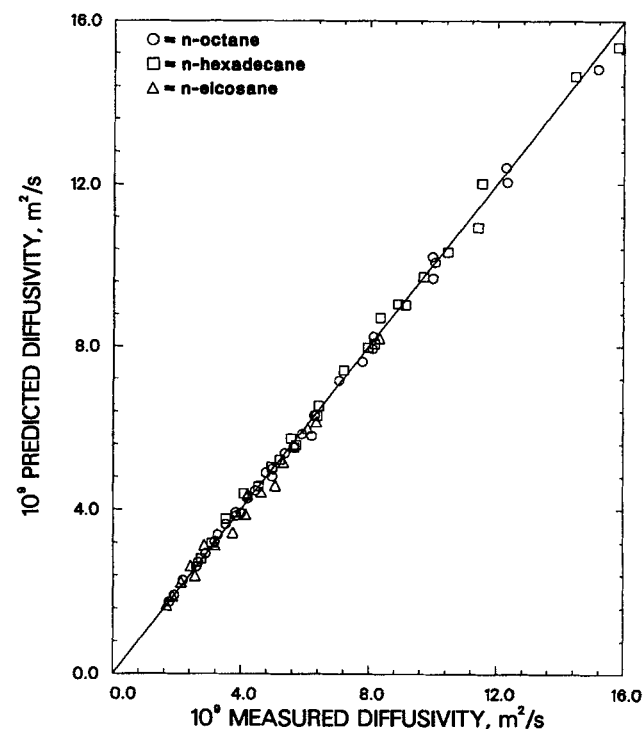


Figure 3. Measured vs. predicted diffusivities.

tetradecane in *n*-hexadecane, and octane to hexadecane in *n*-eicosane. The agreement is excellent and the average error is 2.8%.

As the solute molecules become smaller than *n*-propane, the amount of coupling starts to increase in *n*-octane (Erkey and

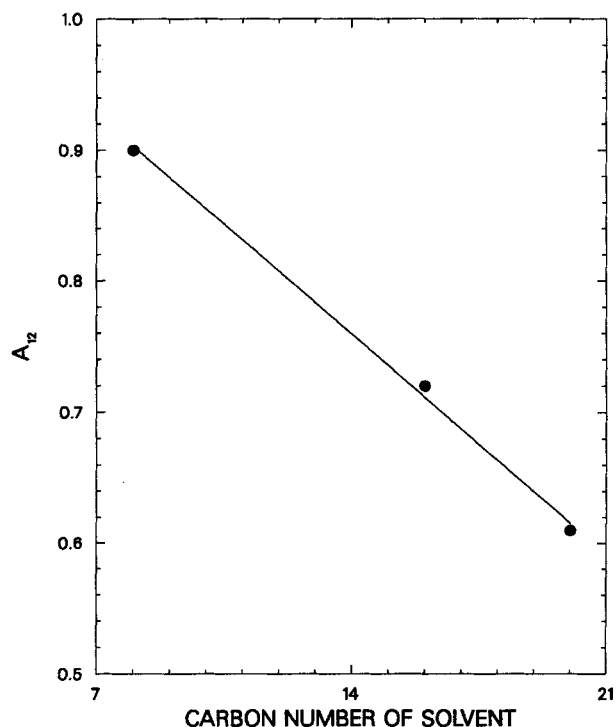


Figure 2. Variation of coupling parameter with carbon number of solvent molecule.

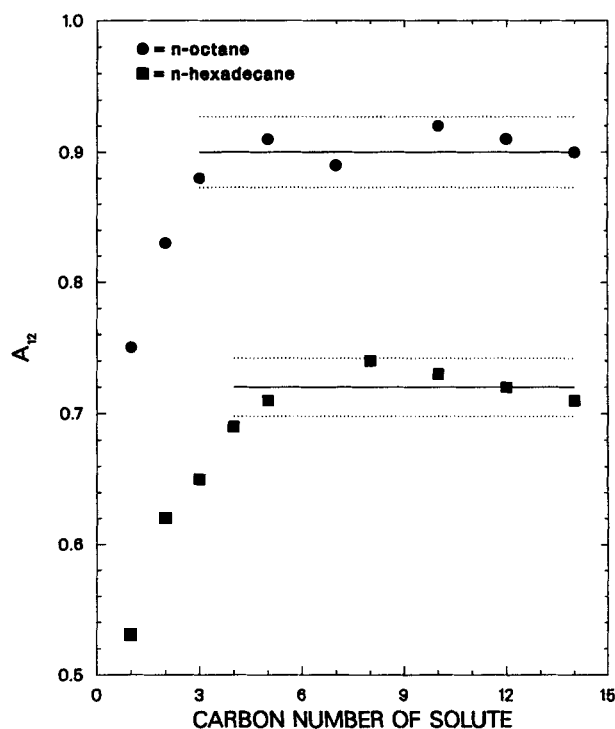


Figure 4. Variation of coupling parameter with carbon number of solute molecule.

Table 3. Closed-Packed Hard-Sphere Volumes, Correction Factors, and Translational-Rotational Coupling Parameters for Diffusion of *n*-Hexane Isomers in *n*-Heptane at 298 K

	$10^9 D_{12}$ m ² /s	$10^6 V_o$ m ³ /mol	$(D_{12,SHS}/D_{12,E}) A_{12}$	
<i>n</i> -hexane	3.17	80.50	0.70	0.94
3MP*	3.06	81.67	0.70	0.89
23DMB**	2.94	83.57	0.70	0.88
22DMB†	2.74	85.25	0.70	0.83
<i>n</i> -heptane	3.00	94.00	—	—

*3-methylpentane

**2,3-dimethylbutane

†2,2-dimethylbutane

Akgerman, 1989). The same behavior is also observed for *n*-hexadecane, where the increase starts as the solute molecules become smaller than butane. This is illustrated in Figure 4, where the coupling parameter for each solute-solvent pair is plotted as a function of carbon number of solute molecule in *n*-octane and *n*-hexadecane. The dashed lines represent $\pm 3\%$ deviation from the mean values. We have previously attributed this phenomena to the increasing sphericity of the solute molecules by comparing the A_{12} values obtained for diffusion of xenon and carbon tetrachloride in *n*-octane to methane in *n*-octane, all of which are spherical solutes with considerably different mass and size ratios. For further investigation of the effect of shape of the solute molecules on the amount of translational rotational coupling, the recent diffusivity measurements of Padrel de Oliveira et al. (1988) were analyzed. The solutes were isomers of *n*-hexane ranging from nonspherical hexane to nearly globular 2,2-dimethylbutane. The solvent was *n*-heptane and the measurements were performed at 298 K. The V_o values, the correction factors, and A_{12} values are given in Table 3. Since all the solutes have the same mass, such a study enables one to separate the effects of mass from size and shape on the coupling parameter. The A_{12} value of 0.94 for *n*-hexane is consistent with the findings presented in this study that the amount of coupling is small for *n*-alkanes smaller than *n*-hexane. Extrapolation of Eq. 10 to *n*-heptane gives a value of 0.93 for the coupling parameter com-

Table 4. Closed-Packed Hard-Sphere Volumes, Correction Factors, and Translational-Rotational Coupling Parameters for Diffusion in *n*-Hexane at 298 K

	Pressure 10^6 N/m ²	$10^9 D_{12}$ m ² /s	V/V_o	$(D_{12,SHS}/D_{12,E})$	A_{12}
[¹⁴ C]Benzene	0.10	4.71	1.636	0.81	0.97
	18.7	4.12	1.600	0.77	0.96
	44.6	3.43	1.550	0.70	0.97
	88.1	2.81	1.504	0.63	0.98
[¹⁴ C]Carbon Disulphide	0.10	5.84	1.636	0.84	0.92
	40.0	4.36	1.558	0.74	0.91
	102.6	3.22	1.482	0.64	0.93
[¹⁴ C]Acetonitrile	0.10	6.10	1.636	0.74	0.86
	39.1	4.50	1.562	0.65	0.84
	85.9	3.80	1.499	0.58	0.91
[¹⁴ C]Benzene:		$\sigma_1 = 5.11 \times 10^{-10}$ m			
[¹⁴ C]Carbon Disulphide:		$\sigma_1 = 4.09 \times 10^{-10}$ m			
[¹⁴ C]Acetonitrile:		$\sigma_1 = 4.28 \times 10^{-10}$ m			

Table 5. Closed-Packed Hard-Sphere Volumes, Correction Factors and Translational Rotational Coupling Parameters for an Equimolar Binary Mixture of *n*-Hexane and *n*-Octane

Temp. K	$10^9 D_{12}$ m ² /s	$10^6 V_o$ m ³ /mol	V/V_o	$(D_{12,SHS}/D_{12,E}) A_{12}$	
295.0	2.81	94.16	1.561	0.74	0.88
300.0	3.04	93.86	1.576	0.77	0.88
308.0	3.40	93.46	1.599	0.81	0.89
315.0	3.74	93.08	1.620	0.83	0.90
323.0	4.11	92.69	1.645	0.86	0.90
328.0	4.37	92.40	1.661	0.88	0.90

pared to 0.94. Furthermore, the significant decrease of the A_{12} value for the nearly globular 2,2-dimethylbutane compared to the highly nonspherical *n*-hexane suggests that it is the shape of the solute molecule which causes the increase in the amount of coupling between the solute and the solvent molecules for diffusion *n*-alkane solvents. Here, it should be noted that the 2,2-dimethylbutane molecule has an effective diameter larger than the *n*-hexane molecule. Therefore, the significantly lower A_{12} values for methane and ethane molecules can be attributed to their shape rather than their mass-to-size ratios.

The density dependence of the coupling parameter can also be tested using the same approach. For such a test, one needs high pressure diffusion data along an isotherm. Therefore, the tracer diffusion measurements of Dymond and Woolf (1982) in *n*-hexane have been analyzed as described above. The results are presented in Table 4. The data analyzed cover the pressure range 0.1 to 102.6×10^6 N/m² which correspond to a reduced volume range of 1.5 to 1.65. The coupling parameter also seems to be independent of density. Extrapolation of Eq. 10 to *n*-hexane gives an A_{12} value of 0.95 which is consistent with the values 0.97 for the benzene tracer and 0.92 for the carbon disulphide tracer. For the acetonitrile tracer, the slightly lower value of the coupling parameter may possibly be attributed to the asymmetric charge distribution of the solute molecule.

Throughout the previous discussion, the translational-rotational coupling parameters have been calculated for cases where the solute is infinitely dilute in the solvent. The coupling parameters can also be calculated across the entire concentration range provided that the correction factors to Enskog results are available as a function of concentration. Eastaer and Woolf (1984) have performed molecular dynamics simulations for an equimolar mixture of 250 smooth hard spheres. The data cover a reduced volume range of 1.5 to 4.0 with mass ratios in the range 1–10 and size ratios in the range 1–3. The mutual diffusion data of Alizadeh and Wakeham (1982) for equimolar mixtures of

Table 6. Closed-Packed Hard-Sphere Volumes, Correction Factors and Translational Rotational Coupling Parameters for an Equimolar Binary Mixture of *n*-Hexane and *n*-Heptane

Temp. K	$10^9 D_{12}$ m ² /s	$10^6 V_o$ m ³ /mol	V/V_o	$(D_{12,SHS}/D_{12,E}) A_{12}$	
300.0	3.55	87.21	1.604	0.82	0.92
308.0	3.97	86.85	1.628	0.85	0.93
315.0	4.30	86.39	1.648	0.87	0.94
323.0	4.71	86.20	1.674	0.90	0.94
328.0	4.91	85.99	1.690	0.92	0.92
333.0	5.18	85.78	1.706	0.94	0.92

Table 7. Closed-Packed Hard-Sphere Volumes, Correction Factors and Translational Rotational Coupling Parameters for an Equimolar Binary Mixture of *n*-Heptane and *n*-Octane

Temp. K	$10^9 D_{12}$ m ² /s	$10^6 V_o$ m ³ /mol	V/V_o	$(D_{12,SHS}/D_{12,E}) A_{12}$	
308.0	3.05	100.09	1.573	0.77	0.91
323.0	3.64	99.21	1.616	0.83	0.90
333.0	4.07	98.62	1.647	0.87	0.89
343.0	4.53	98.09	1.677	0.90	0.89

hexane-heptane, hexane-octane, and heptane-octane were analyzed to study the concentration dependency of the translational-rotational coupling parameter. The data cover a reduced volume range of 1.56–1.71. The coupling parameters were extracted from experimental data employing Eq. 9. All of these mixtures were treated as ideal and nonideality corrections were not used in the calculations. The results are presented in Tables 5–7. The parameter is independent of temperature for *n*-alkane mixtures and is a function of composition. As a first approximation, the parameter may be obtained from the infinite dilution values by a simple relationship:

$$(A_{12})_{x_1, x_2} = A_{12}x_1 + A_{21}x_2 \quad (11)$$

where A_{12} and A_{21} are the translational-rotational coupling parameters for the infinitely dilute case. The above equation gives a value of 0.93 for *n*-hexane and *n*-octane mixture; 0.94 for *n*-hexane and *n*-heptane mixture; and 0.92 for *n*-heptane and *n*-octane mixture which compare within 3% with the values extracted from experimental data.

Notation

- A = translational-rotational coupling parameter
- D = diffusion coefficient
- $g(\sigma)$ = radial distribution function
- k = Boltzman constant
- m = mass of single molecule
- n = number density
- N = Avagadro's number
- T = absolute temperature
- V = molar volume
- V_o = close packed hard sphere volume

Greek letters

- σ = hard sphere diameter
- ξ = packing fraction for hard spheres

Subscripts

- 1 = solute 1
- 2 = solvent

Superscripts

- E = Enskog
- RHS = rough hard sphere
- SHS = smooth hard sphere

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