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Correlation of High-Pressure Diffusion and Viscosity Coefficients for *n*-Alkanes[1]

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Self-diffusion coefficient and viscosity coefficient data for liquid *n*-alkanes over the whole pressure range at different temperatures are satisfactorily correlated simultaneously by a method which is just an extension of that previously used to apply the smooth hard-sphere theory of transport properties to individual transport coefficients. Universal curves are developed for reduced quantities D^* and η^* as a function of reduced volume. A consistent set of values is derived for the characteristic volume V_0 and for parameters R_D and R_η, introduced to account for effects of nonspherical molecular shape and molecular roughness. On this basis, accurate calculation can be made of self-diffusion and viscosity coefficients for other members of the *n*-alkane series, for which data are at present limited.

KEY WORDS: diffusion; hard-sphere theory; *n*-alkanes; viscosity.

1. INTRODUCTION

It has previously been demonstrated [1–3] that thermal conductivity coefficients and viscosity coefficients of *n*-alkanes over wide ranges of temperature and pressure can, separately, be successfully correlated by methods based on a consideration of the exact hard-sphere theory of transport properties. Unfortunately, values which have been reported for the molecular parameter V_0, the volume of close packing, differ significantly. For example, for *n*-hexane at temperatures close to 323 K, V_0 has been variously given as 71.77 [4], 73.06 [5], and $77.3 \times 10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$ [6] from thermal conductivity data analysis and $72.0 \times 10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$ [7] from viscosity measurements. A preliminary simultaneous fit of viscosity and thermal conductivity coefficients gave a V_0 value of $82.12 \times 10^{-6}\,\mathrm{m^3} \cdot$

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mol^{-1} [8], which is significantly higher than these values and also much larger than the figure of $76.32 \times 10^{-6}\,\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$ given by Harris [9] from fitting self-diffusion data for *n*-hexane at 333 K. For a satisfactory correlation of transport properties of *n*-alkanes using methods based on hard-sphere models, it is essential to establish a consistent set of V_0 values. This is particularly important when this approach is to be used for calculation of transport coefficients at other temperatures or for other members of the series where data are at present limited. It is also preferable to have an agreed set of V_0 parameters before embarking on the correlation of transport properties of liquid *n*-alkane mixtures.

In this paper, a simultaneous fit of self-diffusion and viscosity coefficient data for *n*-alkanes is presented, based on consideration of hard-sphere theories. Thermal conductivity is not included at this stage because increases in pressure have only a relatively small effect on this property and, also, because the effects of internal energy have not yet been exactly quantified.

2. THE CORRELATION METHOD

2.1. Theory

In a dense fluid the physically realistic Van der Waals description is equivalent to the hard-sphere model for transport properties, for which approximate expressions for the coefficients of self-diffusion and viscosity are given by the Enskog theory [10]:

$$(nD_{\mathrm{E}}/n_0 D_0) = 1/g(\sigma) \tag{1}$$

$$\eta_{\mathrm{E}}/\eta_0 = [1/g(\sigma) + 0.8b/V + 0.761g(\sigma)(b/V)^2] \tag{2}$$

where g(σ) is the radial distribution function at contact given by Ref. 11, n is the particle number density, and $b = 2\pi N\sigma^3/3$, where σ is the hard-sphere core diameter. Subscript 0 refers to the low density hard-sphere coefficients.

Corrections to this theory for correlated molecular motions have been calculated [12] by molecular dynamics studies. However, more recent computations of hard-sphere diffusion [13] indicate that extrapolation of the results for an infinite-sized system is significantly smaller than that reported earlier. In the case of viscosity, there are greater uncertainties in the computed corrections associated with the larger computing time necessary for this property. Corrections to the Enskog theory for viscosity and thermal conductivity were therefore determined recently [14] by comparing experimental data for these properties for argon, considered as a smooth hard-sphere system, with predicted values from the Enskog theory and selecting the core sizes that gave closest agreement with the molecular dynamics corrections.

Calculation of viscosity or self-diffusion for any compound at a given temperature and pressure requires just a value for parameter V_0, the volume of close packing of spheres, given by $N\sigma^3/2^{1/2}$. This is conveniently derived by an established curve-fitting procedure [2, 15] based on reduced quantities D^* and η^* defined by the following expressions:

$$D^* = \left(\frac{nD_{\mathrm{SHS}}}{n_0 D_0}\right)\left(\frac{V}{V_0}\right)^{2/3} \tag{3}$$

$$\eta^* = \left(\frac{\eta_{\mathrm{SHS}}}{\eta_0}\right)\left(\frac{V}{V_0}\right)^{2/3} \tag{4}$$

where the smooth hard-sphere coefficients are given by the product of the Enskog values and the corrections to Enskog theory, $D_{\mathrm{SHS}} = D_{\mathrm{E}}(D/D_{\mathrm{E}})_{\mathrm{MD}}$ and $\eta_{\mathrm{SHS}} = \eta_{\mathrm{E}}(\eta/\eta_{\mathrm{E}})_{\mathrm{MD}}$.

Values for D^* and η^* are calculated from theory for different reduced volumes, V/V_0. Values are also calculated from experiment since on substitution of the hard-sphere expressions,

$$D^* = 5.030 \times 10^8 \left(\frac{M}{RT}\right)^{1/2} \left(\frac{D}{V^{1/3}}\right) \tag{5}$$

$$\eta^* = 6.035 \times 10^8 \frac{\eta V^{2/3}}{(\mathrm{MRT})^{1/2}} \tag{6}$$

To determine V_0 for a given compound from self-diffusion data at a given temperature, a plot of $\log D^*$ from experiment versus $\log V$, where V is the molar volume, is superimposed on the curve of $\log D^*$ versus $\log(V/V_0)$ by translation along the x axis. Values for V_0 can similarly be derived by curve fitting using viscosity coefficient data. In Figs. 1 and 2, the theoretical curves are calculated from exact smooth hard-sphere theory, using expressions for the corrections to Enskog theory given by Easteal et al. [13] for diffusion and by Dymond [14] for viscosity. The crosses represent the predicted hard-sphere values using the earlier corrections to Enskog theory [12], and it is important to note the significant difference in density dependence of these predictions. It is essential that all curve fitting should be carried out with respect to the same reference curves and we therefore recommend that the solid lines given here, calculated as described above, be taken as the exact hard-sphere reference curves.

Methane at 140 K is taken as the reference system because accurate diffusion [15] and viscosity coefficient [16] measurements have been made

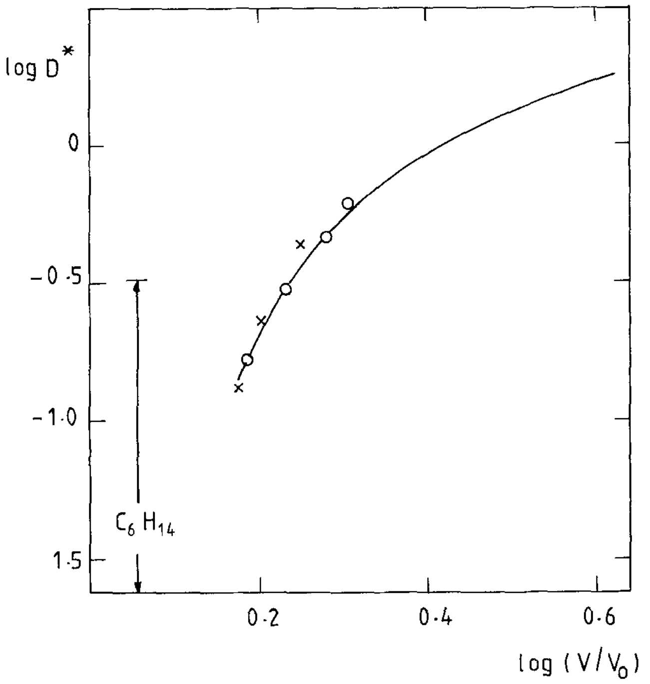

Fig. 1. Variation of log D^* with $\log(V/V_0)$ for hard-sphere systems. D^* is defined by Eq. (3). Solid lines are given by smooth hard-sphere theory with corrections to Enskog theory given by Easteal et al. [13]; (×) corrections given by Alder et al. [12]. (○) Data for methane at 140 K [15]. Vertical lines identify the range of D^* for *n*-hexane.

at this temperature, and this molecule can be expected to behave as a smooth hard sphere with respect to transport properties at high densities. Indeed, it is found [14] that these data can be interpreted on the basis of the smooth hard-sphere model, with the same value for V_0 of $20.825 \times 10^{-6}\,m^3 \cdot mol^{-1}$, as shown in Figs. 1 and 2. Methane data at other temperatures are similarly fitted to the hard-sphere curves, and the derived V_0 values are found [14] to decrease smoothly with increases in temperature as expected since real molecules experience a soft repulsive interaction.

At high densities the hard-sphere system becomes metastable, but for real fluids still higher values for η^* and lower values for D^* are possible, as shown for *n*-hexane in Figs. 1 and 2. Such molecules are generally nonspherical and also exhibit roughness, that is, there is the possibility of transfer of rotational as well as translational momentum on collision. In the case of spherical molecules, Chandler [17] has shown that at suf-

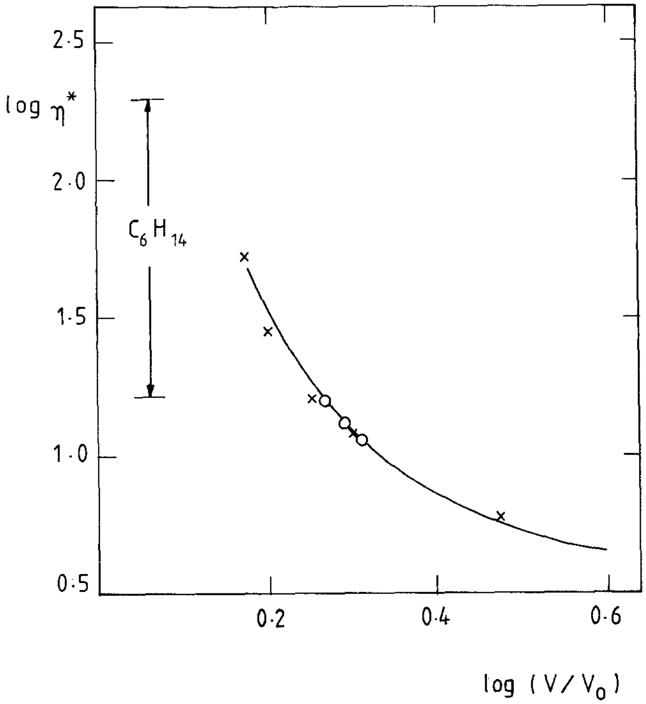

Fig. 2. Variation of log η^* with log(V/V_0) for hard-sphere systems. η^* is defined by Eq. (4). Solid lines are given by smooth hard-sphere theory with corrections to Enskog theory given by Dymond [14]; (×) corrections given by Alder et al. [12]. (○) Data for methane at 140 K [16]. Vertical lines identify the range of η^* for *n*-hexane.

ficiently high densities the rough hard-sphere coefficients are proportional to the smooth hard-sphere coefficients:

$$D_{\mathrm{RHS}} = AD_{\mathrm{SHS}} \tag{7}$$

$$\eta_{\mathrm{RHS}} = C\eta_{\mathrm{SHS}} \tag{8}$$

where $A \leqslant 1$ and $C \geqslant 1$. These translational–rotational coupling factors are supposedly density independent and are assumed to have at most a very weak temperature dependence.

On the basis of this model, assuming temperature independence of A and C, correlation of these transport coefficients for a given compound can be achieved by superimposing plots of log D^* versus log V, and similarly of log η^* versus log V, on the respective curves for a selected reference temperature. This is illustrated in Fig. 3 for the *n*-hexane diffusion coefficient measurements of Harris [9], which cover the temperature range 223 to

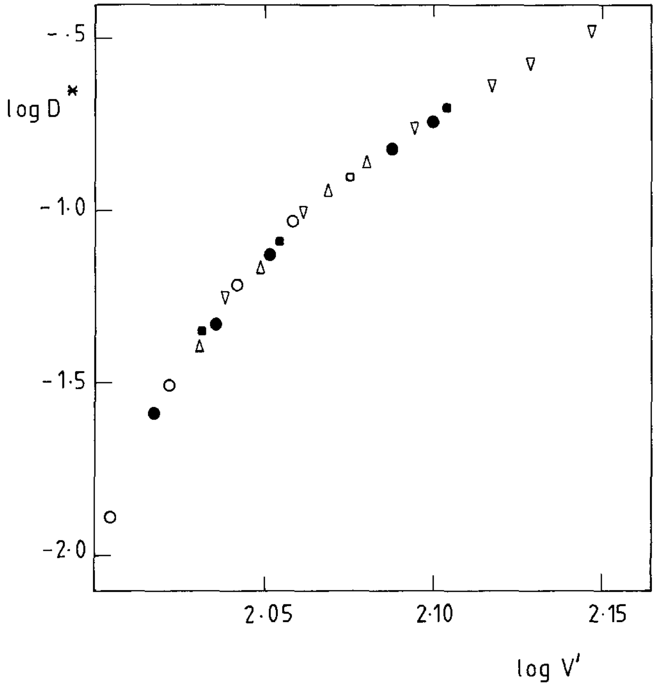

Fig. 3. Correlation of self-diffusion coefficient data [9] for *n*-hexane, based on the 298 K isotherm. $V' = V[V_0(298)/V_0(T)]$, where V is molar volume. (○) 223 K; (△) 248 K; (●) 273 K; (■) 298 K; (▽) 333 K.

333 K. The 298 K isotherm is taken as reference and the required shift along the x axis in order to superimpose the other curves gives the ratio of V_0 values for the different temperatures. These vary smoothly with temperature [9]. (It should be noted that, in terms of the model, there is no evidence of a temperature dependence for A.) Similar results have been obtained from viscosity coefficient measurements for individual *n*-alkanes, and this is now an established method [18, 19] for testing the consistency of experimental viscosity measurements.

In order to determine absolute values for V_0 for different *n*-alkanes, the correlated curves for a given compound are compared with the appropriate smooth hard-sphere curve. To allow for the fact that higher *n*-alkanes are nonspherical, the above ideas can be extended to give

$$D = R_D D_{SHS} \tag{9}$$

$$\eta = R_\eta \eta_{SHS} \tag{10}$$

where the factors R_D and R_η account for nonspherical shape and translational–rotational coupling. Values for these parameters for a given compound are derived by simultaneously curve-fitting the correlated $\log D^*$ versus $\log V$ curve with the solid line in Fig. 1, and the correlated $\log \eta^*$ versus $\log V$ curve with the solid line in Fig. 2. Since horizontal and vertical adjustments are possible, there is a range of values for V_0 at the reference temperature and, also, for R_D and R_η.

2.2. Application

The first conclusion which results from applying the above procedure to *n*-hexane viscosity and self-diffusion coefficients is that it is not possible to obtain a simultaneous fit of both properties with the same V_0 for the reference temperature with R_D and R_η set equal to unity.

To determine the possible range of values for V_0, conditions similar to those which pertain to the translational–rotational coupling factors have been applied, namely, that $R_D \leqslant 1$ and $R_\eta \geqslant 1$. Matching the correlated diffusion curves for *n*-hexane with Fig. 1 to give agreement within 3% leads to the conclusion that V_0 at 298 K, the reference temperature, lies between 76.9 and $80.4 \times 10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$ with R_D between 0.77 and 1.0. From the corresponding viscosity coefficient data fit, V_0 must be between 79.4 and $81.8 \times 10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$ and R_η has limits of 1.0 and 1.33, to fit the data within the estimated experimental uncertainty. For a simultaneous fit of these two properties V_0 for *n*-hexane at 298 K must lie between 79.4 and $80.4 \times 10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$ with $1.33 > R_\eta > 1.16$ and $0.92 < R_D < 1.0$. Similarly, limits can be found for R_D, R_η, and V_0 at the reference temperature for other *n*-alkanes for which self-diffusion and viscosity coefficient values are available. It is found for the accurate *n*-hexane self-diffusion coefficient data [9] and the less accurate diffusion coefficients for other *n*-alkanes [20, 21] that, in terms of the model, effects of nonspherical molecular shape and roughness are very small, and indeed, R_D may be set equal to unity. The corresponding V_0 values lie in the middle of the range determined from a fit of viscosity data alone. We have accordingly taken R_D as 1.0 and determined by curve fitting the optimum V_0 and R_η values that give the best simultaneous fit to the hard-sphere viscosity and diffusion curves. This curve fitting has been carried out graphically but the next stage is to apply numerical techniques with appropriate weighting of the individual points for the two properties.

Values which have been obtained for V_0 are given in Table I. As expected, the V_0 values at a given temperature vary smoothly with changes in the *n*-alkane carbon number. This makes possible an accurate estimation of V_0 for other members of this series. The factor R_η also varies smoothly

Table I. Values for the Characteristic Volume V_0 (in $10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$)

T(K)	90	95	100	110	120	130	140	150
CH_4			22.46		21.57		20.82	
C_2H_6			34.59	34.10	33.70	33.32		32.69
C_3H_8	50.95	50.40	49.82	48.95			47.01	
C_4H_{10}							61.25	60.50
T(K)	160	170	180	200	250	290	300	320
CH_4		19.93	19.69	19.26	18.51		18.00	
C_2H_6				31.52	30.75	30.27		29.94
C_3H_8							42.67	
C_4H_{10}	59.84		58.86	58.17	56.59		55.19	
T(K)	223.2	248.2	273.2	298.2	323.2	348.3	373.2	
C_6H_{14}	84.34	82.64	81.32	80.40	79.64	78.91	78.23	
C_8H_{18}				109.0	107.1	105.5	104.4	
$C_{12}H_{26}$				165.8	163.3	160.9	158.6	
$C_{16}H_{34}$				224.4	221.1	217.6	214.2	

with increases in the carbon chain length for the *n*-alkanes, going from 1 for methane to 1.2 for *n*-octane and then rising more rapidly to just above 1.6 for *n*-hexadecane. Accurate interpolation is possible for other *n*-alkanes.

Once V_0 and R_η have been determined, with R_D equal to 1.0, universal curves can be built up for $\log D^*$ versus $\log V_r$ and for $\log \eta^*$ versus $\log V_r$, where V_r is the molar volume under given conditions multiplied by 20.825, the V_0 value for methane at the reference temperature of 140 K, divided by V_0 for the compound at the experimental temperature. These curves have been represented by polynomials in $(1/V_r)$:

$$\log \eta^* = 0.877 - 78.97/V_r + 7130.4/V_r^2 - 219020/V_r^3 + 3075840/V_r^4 \tag{11}$$

$$\log D^* = 3.285 - 661.04/V_r + 57700/V_r^2 - 2575677/V_r^3 + 56074080/V_r^4 - 490561075/V_r^5 \tag{12}$$

Although this is arguably not the best form of representation, it is considered suitable for determining the degree to which the experimental data can be fitted. For methane, there is a very satisfactory fit of both self-diffusion coefficient and viscosity coefficient measurements, with the agreement with experimental values generally well within 3%. The V_0 values were taken from Table I.

In the case of *n*-hexane, the other *n*-alkane for which extensive accurate viscosity and self-diffusion measurements have been made, the

Table II. Comparison of Self-Diffusion Coefficients Calculated by the Present Method with Experimental Values

	No. of points			
		Deviation from expt.		
	Total	5–10%	>10%	Ref. No.
CH_4	54	6	—	15, 22
C_4H_{10}	19	6	8	20, 21
C_6H_{14}	54	4	—	9
C_6H_{14}	21	3	6	20, 21
$C_{10}H_{22}$	25	6	4	20, 21

experimental values are compared with values calculated from Eqs. (11) and (12), with V_0 values from Table I. For diffusion there is excellent agreement with the results of Harris [9] and also reasonable agreement with those of Bachl and Ludemann [20, 21], for which the reliability is quoted as 10%, at temperatures of 240 K and above. However, at 214 K the experimental values are on average about 15% higher than calculated. Since this isotherm is close to the 223 K isotherm for which Harris reported measurements, it appears that there is some inconsistency in these data.

A summary of the data fit for the *n*-alkanes is presented in Table II for diffusion and in Table III for viscosity. Some of the diffusion coefficient measurements of Bachl and Ludemann show deviations of more than 10%, but some of the discrepancy may be due to the fact that the corresponding

Table III. Comparison of Viscosity Coefficients Calculated by the Present Method with Experimental Values

	No. of points				
		Deviation from expt.			
	Total	5–10%	>10%	Max. dev. (%)	Ref. No.
CH_4	107	—	—	3.1	16
C_2H_6	98	—	—	3.3	24
C_3H_8	60	5	—	6.5	25
C_4H_{10}	79	—	—	3.4	26
C_6H_{14}	37	—	—	3.5	18
C_8H_{18}	41	11	1	11.2	27
$C_{12}H_{26}$	31	7	1	16.6	27
$C_{16}H_{34}$	28	—	—	4.7	18

experimental densities are not available. In this case, densities were calculated from the modified Tait equation by the method of Dymond and Malhotra [23], with an estimated uncertainty of 0.2%. This method is restricted to temperatures below the critical temperature, and higher temperature diffusion coefficient data of Bachl and Ludemann were therefore not considered.

For viscosity, the agreement between calculated and experimental coefficients is generally extremely satisfactory, with only 2 points of 481 deviating by more than 10% from the calculated values. For *n*-alkanes from methane to hexane, the agreement is better than 3% in practically all cases. For higher *n*-alkanes, there are larger discrepancies which may be due in part to the greater uncertainty in the measured density.

3. CONCLUSIONS

It is shown that a simultaneous fit is possible for self-diffusion coefficient and viscosity coefficient data of *n*-alkanes up to elevated pressures by a correlation method based on consideration of the exact hard-sphere theory of transport properties. Universal curves are developed for reduced quantities D^* and η^*, by extension of the hard-sphere results. Values for the equivalent hard-sphere close-packed volume V_0 and factors R_D and R_η which are introduced to account for effects of nonspherical molecular shape and molecular roughness on diffusion and viscosity, respectively, are determined by graphical curve fitting. It is found that both R_D and R_η can be considered temperature independent as well as density independent. While it is not possible to establish unique sets of values for these parameters, they can be fairly closely defined. R_D is very close to unity for the *n*-alkanes and has been taken as exactly 1.0. On this basis, values are given for R_η and for V_0 at the various temperatures. It is found that R_η increases smoothly from 1.0 for methane up to slightly higher than 1.6 for *n*-hexadecane. V_0 values for *n*-alkanes at a given temperature show a smooth variation with the length of the carbon chain.

A consistent set of parameters has been provided which, together with the equations for the universal curves, will allow accurate prediction of these transport properties at elevated pressure for other *n*-alkanes from methane to hexadecane for which data are at present not available.

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