

Composition Dependence of Binary Diffusion Coefficients in Alkane Mixtures

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The binary diffusion coefficients of mixtures of *n*-heptane with *n*-hexane and 2,2,4-trimethylpentane with *n*-hexane have been measured at various compositions at 308.1, 312.2, and 316.5 K using the Taylor dispersion technique. The experimental results for the *n*-hexane/*n*-heptane system were in good agreement with the literature values (<1.5%). The observed binary diffusion coefficients for this system exhibit a linear dependence on composition. On the contrary, the results of the *n*-hexane/2,2,4-trimethylpentane system reveal an interesting behavior of the composition dependence of the binary diffusion coefficients, presenting a slight maximum, for composition at a molar fraction of *n*-hexane of 0.86. In order to explain this difference in behavior, the influence of branching of molecules on diffusion is discussed. It was found that although the Enskog hard-sphere model for binary diffusion can reproduce the experimental results for the *n*-hexane/*n*-heptane system within 3%, it failed to predict the composition dependence of the *n*-hexane/2,2,4-trimethylpentane system within the experimental accuracy. The results showed that there is significant effect of branching in alkane molecules on the diffusion coefficient. This effect has been quantified using the roughness parameter, which represents the magnitude of coupling between translational and rotational motions.

KEY WORDS: composition dependence; diffusion coefficient; *n*-heptane; *n*-hexane; mixtures; 2,2,4-trimethylpentane.

1. INTRODUCTION

There are many well-established methods for the determination of diffusion in liquids [1]. Among them the Taylor dispersion technique offers the advantages of simplicity and speed and has now been established as an

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absolute method for the measurement of diffusion coefficient of liquids. The instrument employed in this work has been described in detailed elsewhere [2, 3] and has been found to have an accuracy of $\pm 1\%$.

In order to predict the diffusion coefficient accurately, many theoretical approaches have been attempted. Most of the success of these estimating equations, whether founded on theory or empirically determined, has been with small molecules. This is because most of the theoretical approaches are firmly couched in a spherical model.

The rough hard-sphere model for diffusion (and other transport properties) considers the dynamics of molecular collisions between rigid spherical molecules at liquid densities [4–6]. It is the most successful theory for interpreting diffusion data to date. To apply the theory, one needs the hardcore diameter, the translational/rotational coupling constant, and the results of molecular dynamics calculations for the correction due to correlated molecular motions [5].

Branching of a molecule affects both the chemical and the physical properties of the compound. For example, it is well known that branching at the alpha carbon decreases the reactivity of alkyl halides toward S_N2 (bimolecular nucleophilic substitution) reaction. These effects on reaction rates are interpreted with the concept of steric hindrance to attack by the attacking nucleophile. In the case of physical properties, it is known that branched hydrocarbons tend to have lower melting and boiling points than their straight-chain isomers. This is because branched hydrocarbons are generally less compact and hence there is weaker interaction between the molecules. The question is then whether similar trends can be established for diffusion of alkane molecules.

Some earlier studies of the diffusion of hexane isomers in argon [7], of octane and heptane isomers in the gas phase [8, 9] and for the pentane and isopentane mixture also in the gas phase [8] seem to show that the diffusion coefficients increase with increasing branching. However, for butane and isobutane [10, 11], a reverse trend was observed. On the other hand, a study on the effect of pressure and temperature on the self-diffusion coefficients of alkane molecules [12] has shown that the self-diffusion coefficients decrease with increasing branching of the *n*-alkanes.

The recent studies on the influence of branching in the diffusion coefficients of *n*-alkane mixtures initiated by Matos Lopes et al. [13] and by Padrel de Oliveira et al. [14] showed that the presence of methyl groups in 2,2-dimethylbutane decreases the binary diffusion coefficient of this liquid in *n*-heptane by about 15% when compared with diffusion of *n*-hexane. Furthermore, it was also noted that the infinite dilution diffusion coefficients of hexane isomers in *n*-heptane decreases with increasing branching, i.e., hexane > 3-methylpentane > 2,3-dimethylbutane > 2,2-di-

methylbutane [14]. In addition, the branched alkane system also shows an unexpected maximum in the dependence of the binary diffusion coefficient on composition at a molar fraction of about 0.5 [14]. This is in contrast with the diffusion coefficient of *n*-alkane mixtures, which generally exhibits a linear dependence on composition.

In order to confirm this behavior and to assess the effect of branching on diffusion, binary diffusion coefficients of *n*-hexane/*n*-heptane mixture and 2,2,4-trimethylpentane (isooctane)/*n*-hexane mixture at various temperatures were measured as a function of compositions. An attempt was then made to apply the rough hard-sphere model to the description of mass transport in these two systems.

2. THEORETICAL

The rough hard-sphere theory [4–6, 13–18] for transport properties has substantially improved the understanding of diffusion, viscosity, and thermal conductivity. However, most of the applications of hard-sphere theory have been on simple spherical molecules. Currently, the quantitative predictions for polyatomic species are hampered by uncertainties in evaluating the hard-sphere diameter and the translational/rotational coupling factor (or roughness factor) and by the lack of molecular dynamics calculations. Because the qualitative features of the theory have been proven correct for a variety of chemical systems, methods have been proposed for using the rough hard-sphere theory even if the exact parameters needed to apply the theory are unknown. Attempts have also been made to extend the theory to the binary diffusion in mixtures of *n*-alkanes [16] where satisfactory results were obtained.

The Enskog rough hard-sphere model for binary mixture assumes that the kinetic binary diffusion coefficient D_{kin} of a real two-component mixture of hard spheres with masses equal to those corresponding molecules of real fluids at the same temperature, number density, and mole fraction. The kinetic diffusion coefficient, D_{kin} , which is derived from thermodynamic consideration, is closely related to the experimental binary diffusion coefficient, D_{12} , by the following expression:

$$D_{12} = D_{\text{kin}} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right) \quad (1)$$

where γ_1 and x_1 are the activity coefficient and mole fraction of component 1.

The kinetic diffusion coefficient, D_{kin} , is more readily interpreted in terms of molecular properties than the binary diffusion coefficient, D_{12} .

Based on this model, the kinetic binary diffusion coefficient of a binary mixture of dense hard-sphere fluid with no coupling of translation and rotation is given by [5]

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

where n is the particle number density of the fluid, m_i is the molecular mass of species i , and x_i is the mole fraction of species i . σ_{12} is the collision diameter of two hard spheres of molecular diameter σ_1 and σ_2 and is given by

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2$$

g_{12} represents the pair correlation function at contact for unlike spheres. The expressions for calculating g_{12} have been given elsewhere [5].

In order to account for the roughness and correlated collision, two factors A_{12} and C were introduced. The modified expression of Enskog theory for a rough hard sphere is as follows [5]:

$$D_{\text{kin}} = D_{\text{kin}}^{\text{Ens}} C(m_1/m_2, \sigma_1/\sigma_2, x_1, \xi) A_{12} \quad (3)$$

The factor C is a function of the packing fraction ξ and mass and size ratios, m_1/m_2 and σ_1/σ_2 . It is also a linear function of composition, employed by Czwojniak et al. [5] to compensate for the correlated motions in a hard-sphere fluid.

The factor A_{12} was introduced by Chandler [6] to account for the possible exchange of translational and rotational energy. It depends only on the nature of the molecules in the mixture and is assumed to be independent of concentration and temperature. The effect of coupling between rotational and translational energy is to reduce the diffusion coefficient.

From studies of the self-diffusion coefficient, it has been found [19] that the molecular dynamics calculations of the group C/g_{12} can be fitted to a straight line as follows:

$$\frac{V}{V_0} C(\sigma_1, m, V/V_0) \frac{1}{g_{12}} = a \left(\frac{V}{V_0} - b \right) \quad (4)$$

where a and b are constants. V is the molar volume of the liquid mixture and V_0 is the fluid hard-core volume given by

$$V_0 = N\sigma^3/\sqrt{2} \quad (5)$$

with N being the Avogadro's constant. A similar functional form was

assumed to hold for binary diffusion, as suggested first by Chen [20]. Substituting the above equation and Eq. (4) into Eq. (3), we have

$$D_{12} = A_{12} \frac{3}{8n\sigma_{12}^2} \left[\frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right]^{1/2} \frac{1}{V} [a(V - bV_0)] \quad (6)$$

This equation can be further simplified to

$$D_{12}/\sqrt{T} = \beta(V - V_D) \quad (7)$$

where β is a constant and $V_D = bV_0$. The recent molecular dynamic calculations of Esteal and co-workers [21] has shown that diffusion over a wider range of densities can be fitted to the above equation with $b = 1.3509$.

Equation (7) will then serve as the starting point for analysis of experimental diffusion data using the rough hard-sphere model. If a linear relationship is obtained between D_{12}/\sqrt{T} and molar volume, V , for a particular fluid, it would then be possible to determine its molecule core volume, V_0 from the intercept and the parameter β from the slope.

3. RESULTS

The experimental results obtained for the binary diffusion coefficients of mixtures of *n*-heptane/*n*-hexane are listed in Table I. Figure 1 shows the composition dependence of the binary diffusion coefficients of this system along the isotherms, whereas Fig. 2 shows the temperature dependence of the binary diffusion coefficients at various compositions. Since the experimental diffusion coefficients for this system exhibit a linear relationship with composition and temperature within the range of tem-

Table I. Diffusion Coefficients $10^9 D_{12}$ ($\text{m}^2 \cdot \text{s}^{-1}$) for Mixtures of *n*-Hexane/*n*-Heptane

Temperature (K)	Mole fraction of <i>n</i> -hexane				
	1.0	0.75	0.5084	0.2498	0.0
308.1	4.13 ± 0.03	4.03 ± 0.02	3.96 ± 0.03	3.87 ± 0.03	3.75 ± 0.03
312.2	4.34 ± 0.02	4.24 ± 0.04	4.16 ± 0.02	4.04 ± 0.03	3.95 ± 0.03
316.5	4.57 ± 0.04	4.46 ± 0.03	4.37 ± 0.04	5.25 ± 0.03	4.16 ± 0.03

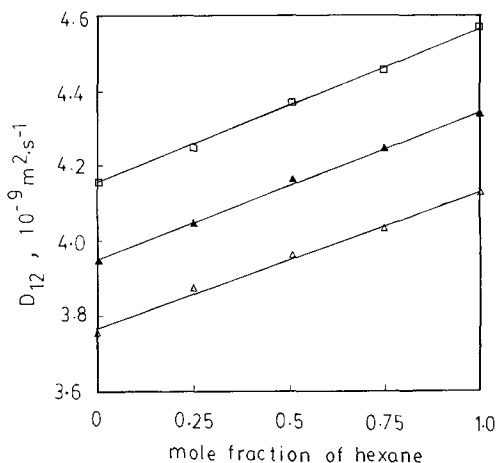


Fig. 1. D_{12} versus composition for the *n*-hexane/*n*-heptane system. Δ , 308.1 K; \blacktriangle , 312.2 K; \square , 316.5 K.

perature studied in this work, it is thus possible to represent the experimental data in the following form:

$$10^9 D_{12}(T, X_{\text{hex}}) = 3.75 + 0.0492(T - 308) + 0.3907X_{\text{hex}} \quad (8)$$

where T and X_{hex} are the temperature in kelvin and molar fraction of *n*-hexane in the mixture, respectively.

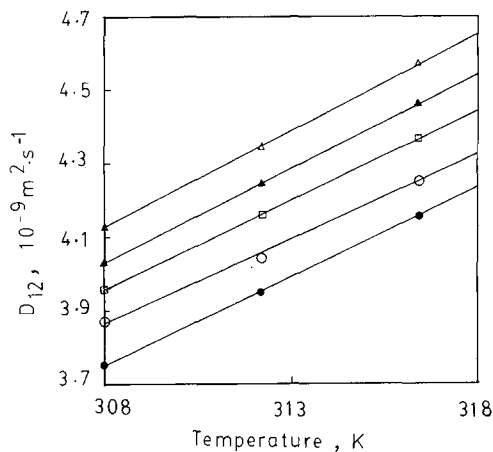


Fig. 2. D_{12} versus temperature for the *n*-hexane/*n*-heptane system. Δ , Pure hexane; \blacktriangle , mole fraction of hexane = 0.75; \square , mole fraction of hexane = 0.5884; \circ , mole fraction of hexane = 0.2498; \bullet , pure heptane.

Table II. Diffusion Coefficients $10^9 D_{12}$ ($\text{m}^2 \cdot \text{s}^{-1}$) for Mixtures of *n*-Hexane/Isooctane

Temperature (K)	Mole fraction of <i>n</i> -hexane					
	0.0	0.2498	0.4992	0.7508	0.8600	1.0
308.1	3.23 ± 0.03	3.30 ± 0.02	3.45 ± 0.01	3.60 ± 0.03	3.66 ± 0.04	3.64 ± 0.04
312.2	3.42 ± 0.04	3.51 ± 0.03	3.62 ± 0.04	3.77 ± 0.03	3.82 ± 0.03	3.81 ± 0.03
316.5	3.62 ± 0.04	3.71 ± 0.03	3.81 ± 0.04	3.96 ± 0.04	—	4.01 ± 0.03

The experimental results obtained for the binary diffusion coefficients of mixtures of *n*-hexane/isooctane are shown in Table II. Figure 3 shows that the diffusion coefficients for the *n*-hexane/isooctane system exhibit a linear dependence on temperature within the temperature range studied in this work.

The composition dependence of the diffusion coefficients of the *n*-hexane/isooctane system shows slight deviation from linearity. Figure 4 illustrates the composition dependence for this system along the isotherms. It was noted that the experimental diffusion coefficients exhibit a nonlinear

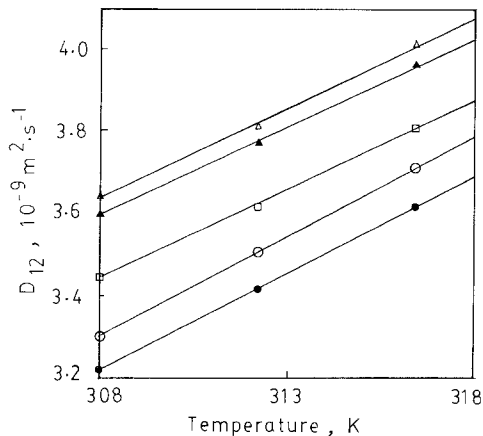


Fig. 3. D_{12} versus temperature for the *n*-hexane/isooctane system. \triangle , Pure hexane; \blacktriangle , mole fraction of hexane = 0.75; \square , mole fraction of hexane = 0.4992; \circ , mole fraction of hexane = 0.2498; \bullet , pure isooctane.

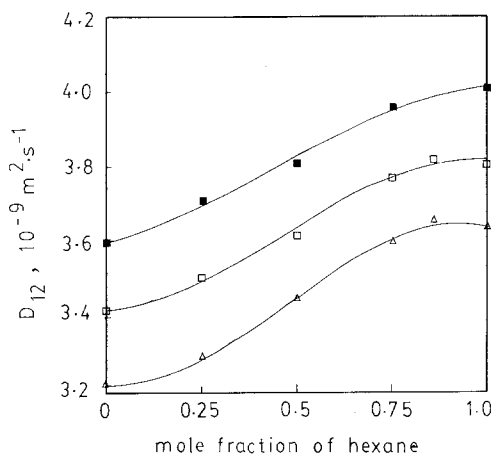


Fig. 4. D_{12} versus composition for the *n*-hexane/isooctane system. Δ , 308.1 K; \square , 312.2 K; \blacksquare , 316.5 K.

relationship on composition. The preliminary results seem to indicate a maximum in the region of $x_{\text{hex}} = 0.86$. This observation is in agreement with data obtained for another branched alkane system, *viz.*, *n*-heptane/2,2-dimethylbutane mixture [13], which exhibits a maximum in the dependence of the binary diffusion coefficient on composition.

Because of the complex nature of the system, it was not possible to represent the experimental data in a simple form as in the case of *n*-hexane/*n*-heptane system with Eq. (8).

4. DISCUSSION

4.1. Interpretation Based on the Hard-Sphere Model

Figure 5 shows the plot of D_{12}/\sqrt{T} for infinite dilution diffusion of heptane in hexane and hexane in heptane, respectively. In Fig. 6, the plots of D_{12}/\sqrt{T} vs V for infinite dilution diffusion of isooctane in hexane and hexane in isooctane are shown. The densities required for the computation of molar volume were obtained from literature [22]. The hardcore volume, V_0 , for the solvent could be obtained graphically by extrapolation, although it should be noted that the long-range extrapolation involved in this procedure can sometimes lead to a large error in the values of V_0 obtained. The hard-sphere diameter (or molecular diameter), σ , could in turn be computed using Eq. (5). The results are summarized in Table III.

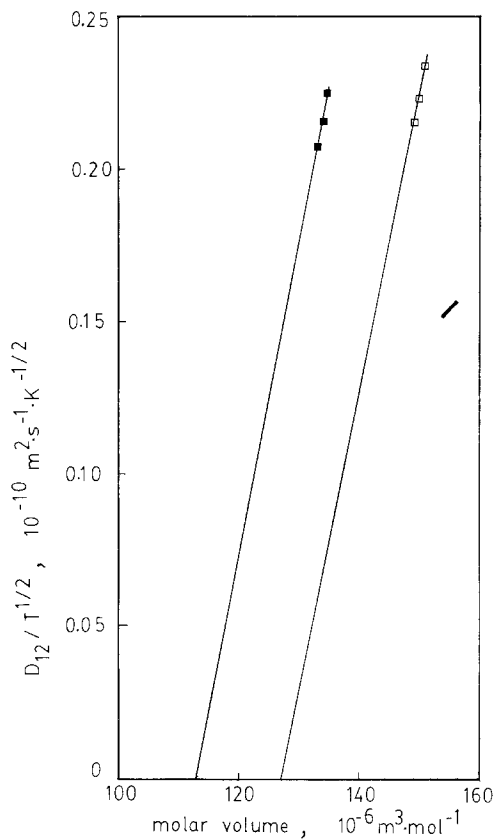


Fig. 5. $D_{12}/T^{1/2}$ versus V . ■, For the *n*-hexane in *n*-hexane/*n*-heptane system; □, for the *n*-heptane in *n*-hexane/*n*-heptane system.

Table III. Values of V_D , V_0 , and σ for *n*-Hexane, *n*-Heptane, and Isooctane

		<i>n</i> -Hexane	<i>n</i> -Heptane	Isooctane
$10^6 V_D$ (m ³)	Present work	113.00 ± 0.04	127.58 ± 0.09	148.80 ± 0.01
$10^6 V_0$ (m ³)	Present work	83.65 ± 0.03	94.44 ± 0.07	110.15 ± 0.01
	Oliveira et al. [14]	82.13 ± 0.08	94.71 ± 0.18	—
$10^{10} \sigma$ (m)	Present work	5.81 ± 0.01	6.05 ± 0.01	6.37 ± 0.01
	Oliveira et al. [14]	5.78 ± 0.01	6.06 ± 0.01	—

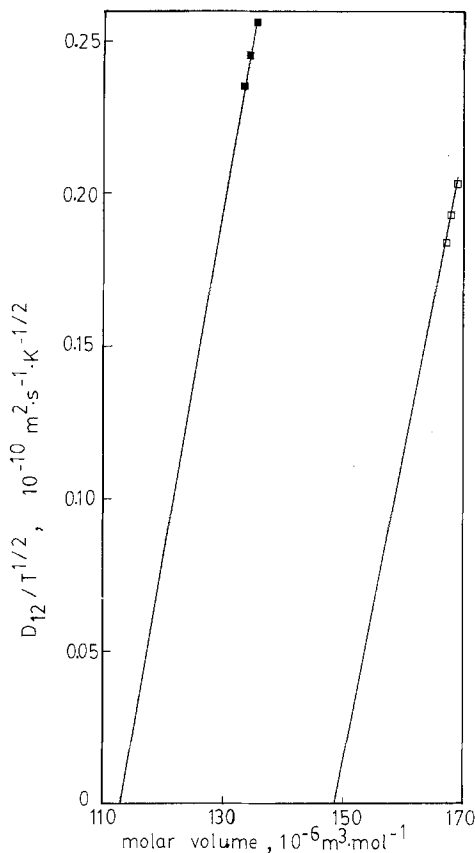


Fig. 6. $D_{12}/T^{1/2}$ versus V . ■, For the n -hexane in n -hexane/isooctane system; □, for the isooctane in n -hexane/isooctane system.

Values for V_0 and σ obtained by Oliveira et al. [14] are also shown in the same table. It is noted that the values of V_0 and σ obtained in the present work for n -hexane and n -heptane are within $\pm 1\%$ agreement with literature values [14]. In the case of isooctane, there is no literature value to compare with.

By a development analogous to that for self-diffusion, it has been shown that

$$\sqrt{T/\eta} = \beta'(V - V_\eta) \quad (9)$$

where η is the measured viscosity; V_η is the molar volume at which the fluidity approaches zero. This quantity is analogous to V_D from diffusivity and hence it serves as an independent check for the accuracy of the hard-core volume V_0 calculated from the experimental data.

The viscosity data required were obtained from literature [22]. From the graph of \sqrt{T}/η versus V , it was found that

$$\begin{aligned} V_\eta \text{ for } n\text{-hexane} &= 115.05 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}, \\ V_\eta \text{ for } n\text{-heptane} &= 134.07 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}, \text{ and} \\ V_\eta \text{ for isooctane} &= 154.25 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}. \end{aligned}$$

The deviation of V_η from V_D for n -hexane is less than $\pm 1\%$ and is thus commensurate with the accuracy of the experimental data. However, the deviations for n -heptane and isooctane exceeded $\pm 2\%$ and are more than the estimated uncertainties associated with the data. Since large extrapolations are required for the determination of V_D and V_η using Eq. (7) and (9), such errors may arise from graphical extrapolation.

The next step of the present investigation is to examine the applicability of the hard-sphere model for the prediction of diffusion coefficients using Eq. (3) [5, 16]. Due to the unavailability of thermodynamic data, it has been assumed throughout the calculations that the experimental diffusion coefficient is equal to the kinetic diffusion coefficient, D_{kin} , within the uncertainty involved. This assumption is equivalent to the statement that the mixtures are ideal. This is certainly a good approximation for the n -hexane/ n -heptane system, since the constituent components in the mixture are rather similar in nature. The error will become more significant for the n -hexane/isooctane system whereby the mixtures are made up of both linear and branched molecules [13].

In view of the above approximation, the experimental diffusion coefficient is then given by:

$$\begin{aligned} D_{12} &= D_{\text{kin}}^{\text{Ens}} \times C \times A_{12} \\ &= D_{12}(\text{pred}) \times A_{12} \end{aligned} \quad (10)$$

where $D_{\text{kin}}^{\text{Ens}}$ is the Enskog kinetic diffusion coefficient from Eq. (2) and $D_{12}(\text{pred})$ is the predicted diffusion coefficient given by the product of $D_{\text{kin}}^{\text{Ens}}$ and C . In the present context, $D_{12}(\text{pred})$ represents a theoretically calculated value based on the hard-sphere model. For the calculation of $D_{12}(\text{pred})$, the following assumptions have been made.

- (1) Molecular diameter and the translational/rotational coupling constant are independent of temperature since the temperature range involved is very small.
- (2) Expressions for constant C [5] are applicable to both systems.

The experimental and predicted diffusion coefficients as well as the values of A_{12} for n -hexane/ n -heptane and n -hexane/isooctane systems are listed in Tables IV and V, respectively. The deviations of the experimental

Table IV. Values of D_{12} (Experimental), D_{12} (Predicted), and A_{12} for *n*-Hexane/*n*-Heptane System

Temperature (K)		Mole fraction of <i>n</i> -hexane				
		0.0	0.2498	0.5084	0.7500	1.0
308.1	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	3.80	3.88	3.98	4.10	4.22
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	3.75	3.87	3.96	4.03	4.13
	A_{12}	0.99	1.00	0.99	0.98	0.98
312.2	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	3.98	4.07	4.19	4.31	4.45
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	3.95	4.04	4.16	4.24	4.34
	A_{12}	0.99	0.99	0.99	0.98	0.98
316.5	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	4.16	4.27	4.40	4.53	4.69
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	4.16	4.25	4.37	4.46	4.57
	A_{12}	1.00	1.00	0.99	0.98	0.97

results from the predicted values based on the hard-sphere model for both systems are graphically presented in Figs. 7 and 8. It is apparent from Fig. 7 that the predicted diffusion coefficients of the *n*-hexane/*n*-heptane system agree with the experimental values to within 3%. Furthermore, it was observed that the translational/rotational coupling constant, A_{12} , for the mixtures lies in the range between 0.97 and 1.00. The values of A_{12} reported in literature for pure hexane and heptane are 0.98 and 0.96 [14], respectively. They were in fair agreement with the values determined in the

Table V. Values of D_{12} (Experimental), D_{12} (Predicted), and A_{12} for the *n*-Hexane/Isooctane System

T (K)		Mole fraction of <i>n</i> -hexane (x_{hex})				
		0.0	0.2497	0.4992	0.7508	1.0
308.1	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	3.02	3.15	3.34	3.62	3.98
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	3.22	3.30	3.45	3.60	3.64
	A_{12}	1.06	1.05	1.03	0.99	0.92
312.2	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	3.19	3.32	3.53	3.82	4.20
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	3.42	3.51	3.62	3.77	3.81
	A_{12}	1.07	1.06	1.03	0.99	0.91
316.5	$10^9 D_{12}(\text{pred})(\text{m}^2 \cdot \text{s}^{-1})$	3.34	3.49	3.72	4.04	4.44
	$10^9 D_{12}(\text{m}^2 \cdot \text{s}^{-1})$	3.62	3.71	3.81	3.96	4.01
	A_{12}	1.08	1.06	1.02	0.98	0.90

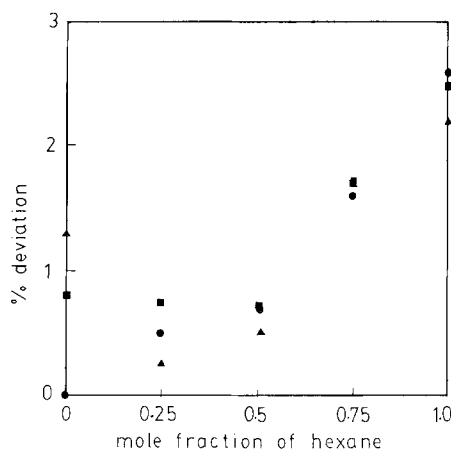


Fig. 7. Percentage deviation of $D_{12}(\text{pred})$ from $D_{12}(\text{experimental})$ for n -hexane/ n -heptane system (% deviation = $[D_{12}(\text{pred}) - D_{12}(\text{exp})]/D_{12}(\text{exp}) \times 100\%$). \blacktriangle , 308.1 K; \blacksquare , 312.2 K; \bullet , 316.5 K.

present work within the experimental uncertainty. Since the A_{12} values are close to unity, this implies that the molecules in this system behave like rigid hard spheres and thus the Enskog hard-sphere model can be applied without much difficulty.

For the n -hexane/isooctane system, the $D_{12}(\text{pred})$ differs from the

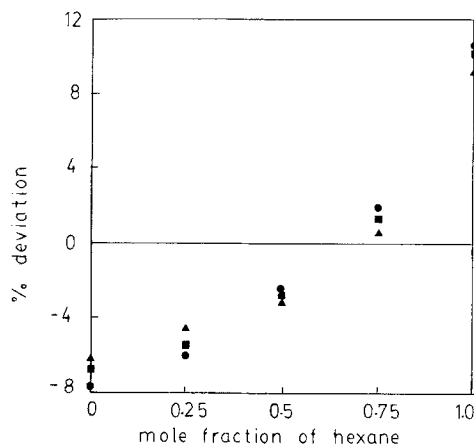


Fig. 8. Percentage deviation of $D_{12}(\text{pred})$ from $D_{12}(\text{experimental})$ for n -hexane/isooctane system (% deviation = $[D_{12}(\text{pred}) - D_{12}(\text{exp})]/D_{12}(\text{exp}) \times 100\%$). \blacktriangle , 308.1 K; \blacksquare , 312.2 K; \bullet , 316.5 K.

experimental values by as much as 11%. Moreover, both positive and negative deviations were observed (Fig. 8). This means that the diffusion of molecules in pure hexane (infinite dilution of isooctane in *n*-hexane) is much slower than would be predicted from the hard-sphere model, while the diffusion of molecules in pure isooctane (infinite dilution of *n*-hexane in isooctane) is considerably faster than would be predicted from the model. In addition, the translational/rotational coupling constant was found to increase drastically from 0.91 for isooctane in *n*-hexane to 1.06 for *n*-hexane in isooctane. Physically A_{12} is expected to be less than unity as a rough molecule diffuses slower than a smooth molecule [6]. However, the value of A_{12} for *n*-hexane in isooctane was found to be greater than unity. This could be due to the dependence of the function C in Eq. (3) on composition. Nevertheless, the above observations reflect that the geometry of the molecules could have significant effects on the coupling between translational/rotational motions.

Another reason for the discrepancy can probably be found in the assumed linearity of the constant C on composition. The present results seem to indicate that this is not an adequate relation which is consistent with what has been observed in the *n*-heptane/2,2-dimethylbutane system [13]. Whether it is a quadratic or exponential function of composition is not known with certainty unless computer dynamic calculations on a suitable model for branched alkanes are carried out. Furthermore, the expression for the constant C used in the computation of the predicted diffusion coefficients is tailored mainly for those cases where the mass and size ratios are close to unity [5]. For the *n*-hexane/isooctane system, the mass and size ratio are 1.33 and 1.10, respectively. Henceforth, the deviation of the experimental results from the predicted values may partly be attributed to the inadequacy of the expressions for calculating C . At this juncture, it is important to point out that any error in the computation of the constant C will be incorporated into the value of A_{12} . Therefore care must be exercised in the formal interpretation of the variation of A_{12} in the system. Nevertheless, the calculated A_{12} values for the cases of infinite dilution are not subjected to error of such nature, in contrast with those A_{12} values from mixtures, since the value of constant C does not depend on composition for pure liquids.

Since the Enskog diffusion coefficient is inversely proportional to the square of the collision diameter, any error in evaluating the molecular diameters of the solvents would result in a large error in the predicted diffusion coefficients. Because experiments were carried out in a fairly narrow temperature range, the molecular diameters required for computation were obtained graphically by extrapolation. Such extrapolated values are inevitably subjected to some uncertainties.

In addition, the discrepancy may also arise from the assumption that the thermodynamic factor, $d \ln \gamma / d \ln x$, in Eq. (1) is unity. This is certainly not a good approximation since isooctane and *n*-hexane are structurally dissimilar. The exact evaluation of this thermodynamic factor will require the measurements of fugacity coefficient as a function of composition.

Another observation is that the difference between the predicted and calculated values is consistently higher at higher temperature, indicating that the molecular diameters used in the computation may be a function of temperature. Currently, the relationship between molecular diameter and temperature in mixtures of normal and branched alkanes is not known with certainty. This problem can be alleviated by performing measurements of diffusion coefficient or viscosity of these mixtures at a wider range of temperature.

4.2. Effect of Branching on Diffusion

Recent spectroscopic investigations and light-scattering experiments [23] with saturated liquid hydrocarbons and their mixtures indicate a specific and distinct influence of the constitution, conformation, and flexibility of the molecule on the structure and macroscopic behavior of such liquids. The orientational order present in pure liquid *n*-alkanes, for example, characteristically affects the thermodynamic mixing properties, such as enthalpy and entropy of mixing, when these liquids are mixed with each other. A thorough understanding of the liquid structure will inevitably assist us in interpreting the observed diffusion coefficients.

Bothorel et al. have shown [24] that the segments of a chain molecule have short-range anisotropic interactions in the liquid phase. They introduced the concept of "correlation of molecular order (CMO)" [24] for the study of the structure of pure liquids and mixtures. Subsequently Heintz and Lichtenthaler [23] have found that CMO occurs particularly with *n*-alkanes ($n > 6$) and is not observed in corresponding isomeric alkanes which are highly branched. When an *n*-alkane molecule is mixed with a globular molecule (e.g., 2,2-dimethylbutane), an abnormally high value of the enthalpy of mixing [24] results since the energetically favoured anisotropy decreases. It therefore seems that the forces that originate the correlation of molecular orientation are due to stereochemical packing phenomena for *n*-alkane chains. This CMO increases with chain length and is smaller for highly branched molecules [14]. In other words, the addition of a comparatively rigid globular molecule to an oriented structure of chain molecules, with dense packing, will create disorder in the liquid phase and, thereby, destroy the preferential parallel orientation of the chain segment [14].

A summary of the experimental data on the infinite dilution diffusion coefficient for mixtures of alkanes is given in Table VI. It can be seen that the diffusion coefficient of isooctane (in *n*-hexane) is lower than that of *n*-octane (in *n*-hexane). This is consistent with what has been observed in the hexane isomer/*n*-heptane systems, in which the diffusion coefficients were found to be systematically decreasing with increasing branching [13, 14]. Such a decrease in diffusion coefficient of branched alkane molecule may be attributed to the breaking of short-range order in the alkane structure due to the diffusion of branched molecules [14]. Because such destruction of order in the liquid structure is known to be energetically unfavourable, the diffusion process becomes slower. The difficulty for the highly branched isooctane molecule in maneuvering through the fairly compact liquid structure of *n*-hexane seems also to result in more significant exchange of translational and rotational energy, leading to a lower observed A_{12} value for *n*-hexane (0.91). Incidentally, this value is reasonably close to the A_{12} value of 0.92 for *n*-heptane in 2,2-dimethylbutane reported in literature [13].

On the other hand, the infinite dilution diffusion coefficient of *n*-hexane in isooctane was found to be higher than that for *n*-hexane in *n*-octane. In order to explain such an observation, the hardcore volume of the solvent must be taken into account. Isooctane molecules, being much larger in size and highly branched, are believed to create much larger voids between molecules as compared to *n*-octane molecules. As a result, the diffusion of small molecule such as *n*-hexane will be greatly facilitated, thus leading to a higher observed diffusion coefficient for isooctane.

Muckenfuss and Curtiss [25] have extensively investigated the kinetic theory of gases composed of molecules which are not spherical in shape.

Table VI. Infinite Dilution Diffusion Coefficients for Alkane Mixtures
(*n*-Hex = Hexane; *n*-Hep = Heptane; *n*-Oct = Octane; 2,2-Dmb = 2,2-Dimethylbutane;
i-Oct = 2,2 + ,4-Trimethylpentane)

Infinite dilution of X in Y		$10^9 D_{12}$ ($\text{m}^2 \cdot \text{s}^{-1}$)	Temp. (K)	Hard-core volume of Y (10^6m^3)	Ref. No.
X	Y				
<i>n</i> -Hex	<i>n</i> -Hep	3.17	298	94.38	13
2,2-Dmb	<i>n</i> -Hep	2.74	298	94.38	13
<i>n</i> -Oct	<i>n</i> -Hex	3.85	308	82.11	26
<i>i</i> -Oct	<i>n</i> -Hex	3.64	308	82.11	This work
<i>n</i> -Hex	<i>n</i> -Oct	2.97	308	105.6	26
<i>n</i> -Hex	<i>i</i> -Oct	3.22	308	109.1	This work

They concluded that the self-diffusion coefficient of such molecules, relative to smooth hard-spheres of the same volume, increases with increasing non-sphericity. A similar result is expected in dense fluids [5].

For those molecules which may be approximately spherical in shape, but whose centers of mass and geometry do not coincide, Sandler and Dahler [26] have shown that such load-sphere structure arrangement increases the diffusion coefficient in the dilute gas relative to that of smooth hard spheres of the same mass and size. Again, a similar result is expected in dense fluids [5].

As mentioned earlier, isooctane molecules are large and highly branched. The effect of nonspherical shape and asymmetric mass distribution in isooctane is expected to result in an increase in the observed A_{12} value. The present results seem to provide further support for the above findings [3, 26, 27].

Since the *n*-hexane and *n*-heptane molecules are comparable in size and unbranched, one would expect the liquid structure of a mixture of *n*-hexane and *n*-heptane to be fairly similar in nature to that of the pure liquids. In other words, the mixture behaves as an ideal one. As a consequence, it is not surprising to observe a linear dependence of diffusion coefficient on composition.

On the contrary, the difference in size between the *n*-hexane and the isooctane molecule is significant. A simple calculation will reveal that the size of the isooctane molecule is about 25% larger than that of *n*-hexane molecule. In addition, the isooctane molecules are highly branched. One would then speculate the liquid structure of *n*-hexane and isooctane mixture to be a more irregular one with large voids between the molecules. The ease of diffusion will then depend very much on the orientation of the molecules in the mixture. The experimental results indicate that as the molar fraction of *n*-hexane increases, the liquid structure of the mixture becomes more compact. Henceforth, the diffusion of molecules becomes increasingly hampered and this will result in a lower observed diffusion coefficient and a lower translational/rotational coupling constant. Consequently, the value of A_{12} for this system exhibits a composition dependency, in contrast with the *n*-hexane/*n*-heptane system. As mentioned earlier, *n*-hexane and *n*-heptane molecules are structurally similar with comparable values of A_{12} (0.98 for *n*-hexane, 1.00 for *n*-heptane), and therefore, the dependency on composition will not be obvious even if it is present. However, the difference of A_{12} for *n*-hexane in isooctane (1.06) and isooctane in *n*-hexane (0.91) is significantly larger in magnitude. Consequently, its variation with composition becomes apparent.

In summary, the experimental results seem to indicate that the observed diffusion coefficient is related to the stereochemical packing of the

liquid structure of the mixture, which in turn depends on the geometry and size of the constituent components. In the light of the above discussions, it is discernible that branching in alkane molecules exerts a significant effect on diffusion.

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