

## Mutual Diffusivity in Binary Mixtures of *n*-Heptane with *n*-Hexane Isomers<sup>1</sup>

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This paper presents a study of the influence of branching in the binary diffusion coefficients of *n*-heptane + *n*-hexane isomers, in the liquid state. The measurements have been made with the Taylor dispersion technique, at several compositions, at 283 and 298 K, for the *X* + *n*-heptane mixtures, where *X* = *n*-hexane, 3-methylpentane, 2, 3-dimethylbutane, and 2, 2-dimethylbutane. The results show a very interesting behavior of the composition dependence of the binary diffusion coefficients, presenting a maximum, for compositions about a molar fraction of *n*-heptane of 0.5, which increases with the increase in the degree of branching, suggesting the possibility of order-disorder effects caused by stereochemically favored packing in the liquid phase and energetically favored segment interaction in the liquid mixtures. An attempt to apply the van der Waals model to these data could not predict the experimental binary diffusion coefficients of these systems within the experimental accuracy.

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**KEY WORDS:** binary diffusion; 2,2-dimethylbutane; 2,3-dimethylbutane; *n*-heptane; *n*-hexane; liquid mixtures; 3-methylpentane; Taylor dispersion.

### 1. INTRODUCTION

In recent years, we have developed an instrument to measure binary diffusion coefficients in liquid mixtures using the Taylor dispersion method [1]. It has been successfully applied to binary diffusion and infinite dilution diffusion coefficients of *n*-alkane mixtures, as well as to H<sub>2</sub>O + D<sub>2</sub>O, often considered as a reference system [2]. It has been shown that the Taylor dispersion method is capable of producing data with an accuracy of  $\pm 1\%$ ,

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if the apparatus design obeys the constraints imposed by the theory of the method [3].

The transport of mass in binary systems depends either on the molecular energies involved in the motion of molecules and on the mass differences of the diffusing species. In order to try to separate these two effects, a study on the influence of branching in the diffusion coefficients of *n*-alkane liquid mixtures was initiated in this laboratory and results obtained for the system 2,2-dimethylbutane + *n*-heptane at 297 K have been presented [4], together with the application of the van der Waals model of transport in binary liquid systems [5–7].

The preliminary study showed that the presence of methyl groups in 2,2-dimethylbutane decreased by about 15% the binary diffusion coefficient of this liquid in *n*-heptane, compared with the diffusion of *n*-hexane. It has also shown an unexpected maximum in the dependence of the binary diffusion coefficient on composition.

In order to confirm this behavior the binary diffusion coefficient in *n*-heptane + *X* mixtures, where *X* is the *n*-hexane isomers, namely, *n*-hexane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane at 298 K, has been measured as a function of composition. Two systems were also studied at 283 K to assess the effect of temperature on the diffusional behavior, namely, *n*-heptane and *n*-hexane + 2,3-dimethylbutane.

## 2. EXPERIMENTAL TECHNIQUE

The Taylor dispersion technique is based on the dispersion of a pulse of an injected mixture in a laminar flowing stream of slightly different composition. For the sake of brevity the reader is referred to Refs. 1–4 for a detailed description of the apparatus used in this study and the evaluation of the experimental diffusion coefficients.

The mixtures of the *n*-alkanes were prepared from the pure liquids (supplied by Fluka AG), degasified, and distilled. The purity of the liquids was assessed by gas chromatography and was in excess of 99.4%. The mixtures were prepared gravimetrically with an error which is estimated to be inferior to 0.0001. Times of the order of 4 ks were used in the measurements and the moments of the Gaussian concentration curve were measured to 0.002% (first) and 0.08%. It is estimated that the overall accuracy of the measurements is better than 1%.

## 3. RESULTS AND DISCUSSION

Tables I to III display the results obtained for the different systems.

In a previous paper [4] the infinite dilution diffusion coefficients of

**Table I.** Binary Diffusion Coefficients for the System *n*-Hexane(1) + *n*-Heptane(2)

<i>T</i> = 283 K		<i>T</i> = 298 K	
<i>x</i> <sub>2</sub>	10 <sup>9</sup> <i>D</i> <sub>12</sub> (m <sup>2</sup> · s <sup>-1</sup> )	<i>x</i> <sub>2</sub>	10 <sup>9</sup> <i>D</i> <sub>12</sub> (m <sup>2</sup> · s <sup>-1</sup> )
0.0088	3.14 <sub>9</sub> ± 0.03	0.0032	3.72 <sub>4</sub> ± 0.04
0.2523	3.00 <sub>3</sub> ± 0.03	0.2559	3.65 <sub>9</sub> ± 0.04
0.5015	2.93 <sub>9</sub> ± 0.03	0.5014	3.57 <sub>9</sub> ± 0.04
0.7480	2.82 <sub>5</sub> ± 0.03	0.7487	3.44 <sub>2</sub> ± 0.03
0.9979	2.67 <sub>5</sub> ± 0.03	0.9969	3.17 <sub>9</sub> ± 0.03

**Table II.** Binary Diffusion Coefficients for the System 2,3-Dimethylbutane (1) + *n*-Heptane (2)

<i>T</i> = 283 K		<i>T</i> = 298 K	
<i>x</i> <sub>2</sub>	10 <sup>9</sup> <i>D</i> <sub>12</sub> (m <sup>2</sup> · s <sup>-1</sup> )	<i>x</i> <sub>2</sub>	10 <sup>9</sup> <i>D</i> <sub>12</sub> (m <sup>2</sup> · s <sup>-1</sup> )
0.0025	2.82 <sub>7</sub> ± 0.03	0.0031	3.34 <sub>0</sub> ± 0.03
0.2526	2.78 <sub>1</sub> ± 0.03	0.2701	3.32 <sub>8</sub> ± 0.03
0.4989	2.82 <sub>1</sub> ± 0.03	0.5020	3.34 <sub>7</sub> ± 0.03
0.7527	2.63 <sub>2</sub> ± 0.03	0.7511	3.28 <sub>4</sub> ± 0.03
0.9976	2.39 <sub>9</sub> ± 0.02	0.9974	2.94 <sub>3</sub> ± 0.03

**Table III.** Binary Diffusion Coefficients for the Systems 3-Methylpentane (1) + *n*-Heptane (2) and 2,2-Dimethylpentane (1) + *n*-Heptane (2) at 298 K

System	<i>x</i> <sub>2</sub>	10 <sup>9</sup> <i>D</i> <sub>12</sub> (m <sup>2</sup> · s <sup>-1</sup> )
3-MP + <i>n</i> -HEP	0.0032	3.74 <sub>4</sub> ± 0.04
	0.2543	3.66 <sub>3</sub> ± 0.04
	0.5016	3.50 <sub>9</sub> ± 0.04
	0.7523	3.45 <sub>5</sub> ± 0.03
	0.9972	3.06 <sub>4</sub> ± 0.03
2,2-DMB + <i>n</i> -HEP	0.0027	3.08 <sub>6</sub> ± 0.03
	0.2543	3.14 <sub>3</sub> ± 0.03
	0.5018	3.17 <sub>1</sub> ± 0.03
	0.7526	3.05 <sub>7</sub> ± 0.03
	0.9972	2.74 <sub>7</sub> ± 0.03

*n*-heptane in *n*-hexane at 297 K were compared with available data obtained by other authors. The measurements were repeated at a slightly higher temperature (298 K) and a value of  $(3.72 \pm 0.04) \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  was obtained. For comparison, this result was corrected to 297 K, assuming a linear dependence [8, 9] of the logarithm of  $D_{12}^0$  with reciprocal temperature in the interval 283 to 298 K. The value obtained,  $3.68 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ , agrees within the experimental accuracy with the value  $3.66 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  previously reported [4].

Figure 1 shows the binary diffusion coefficients for the four systems studied at 298 K as a function of the molar fraction of *n*-heptane. It is shown that the binary diffusion coefficient systematically decreases with increasing degrees of branching of the alkane. The figure also shows that there is a maximum in the composition dependence when one of the diffusing molecules is highly branched (2,2-dimethylbutane and 2,3-dimethylbutane). It can also be seen that this behavior seems to disappear when branching is reduced to one methyl group (3-methylpentane).

Recent spectroscopic and light-scattering studies [10] with liquid alkanes show a distinct influence of the constitution, conformation, and flexibility of the molecule in the structure of the liquid phase and, consequently, in the thermodynamic properties. No systematic studies were found for the transport properties in the liquid phase, although it has been found in this laboratory that the branching significantly decreases the thermal conductivity of *n*-alkanes [11]. However, it is well known that any

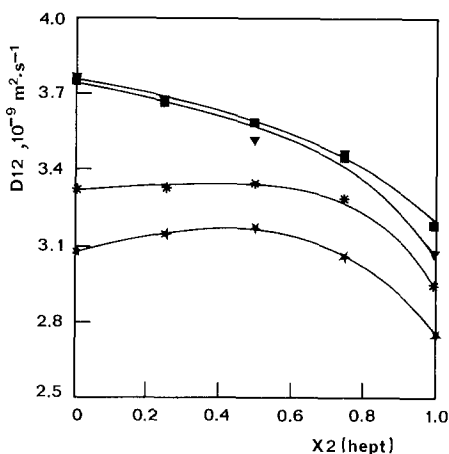


Fig. 1. The binary diffusion coefficients of  $X + n$ -heptane systems at 298 K. (■)  $X = n$ -hexane; (▼)  $X = 3$ -methylpentane; (\*)  $X = 2,3$ -dimethylbutane; (★)  $X = 2,2$ -dimethylbutane.

diffusion process, including translational, rotational, and vibrational motions of the molecules, is a strong probe of structural effects.

Some earlier studies of the diffusion of hexane isomers in argon [12], of octane and heptane isomers [13, 14], and of the pentane + isopentane mixture in the gas phase [15] seem to show that the diffusion coefficients increase with increasing branching. However, Muckenfuss and Curtiss' [16] kinetic theory analysis of a gas composed of spherocylinders showed that nonsphericity increased the self-diffusion coefficient of a spherocylinder molecule relative to smooth-hard spheres of the same volume, a result found experimentally for the system butane + isobutane [15, 17]. Czwozniak et al. [7] state that a similar theoretical result can apply in principle to diffusion in dense fluids.

A recent study on the effect of pressure and temperature on the self-diffusion coefficients of alkane molecules [18, 19] has shown that the self-diffusion coefficients decrease with increasing branching of the *n*-alkanes and that for 2-methylpentane and 2,2- and 2,3-dimethylbutane, the sterical crowding of the methyl groups leads to a stronger temperature dependence of the self-diffusion coefficients, increasing with pressure.

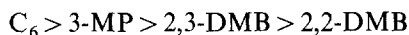
These results seem to agree with the values herein reported. The self-diffusion coefficients obtained for 2,2- and 2,3-dimethylbutane are close to the values of the infinite-dilution diffusion coefficients in *n*-heptane, and although no straight comparison between two different diffusion coefficients can be made, they follow the general behavior found for other systems [9].

In binary liquid systems mass transport is influenced by mass and energy effects, as a diffusing molecule is perturbed by the potential field created by its next neighbors. In the mutual diffusion in mixtures of isomers, the mass effects are negligible, so that the process is possibly influenced only by the shape and conformation of the molecules and, therefore, by the structure of the liquid phase.

It has been shown previously that the segments of a chain molecule have short-range anisotropic interactions in the liquid phase, usually quantified by the "correlation of molecular order" (CMO), first introduced by Bothorel et al. [20] to study the structure of pure liquids and mixtures. The extension of this concept to the interpretation of thermodynamic properties of mixtures of *n*-alkanes was done by Patterson et al. [21–23]. According to Heintz and Lichtenthaler [10], CMO occurs particularly with *n*-alkanes ( $n > 6$ ) and is not observed for corresponding isomeric alkanes which are highly branched [21, 24].

When an *n*-alkane molecule is mixed with a globular molecule (e.g., 2,2-dimethylbutane), the energetically favored orientation of the segments is destroyed and the optical molecular anisotropy decreases, originating an

abnormally high value of the enthalpy of mixing [10]. 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. 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, destroying the preferential parallel orientation of the chain segment, which is energetically favored. In the absence of a quantitative explanation for the diffusivity results shown above, it is interesting to note that some of the features of the experimental data seem to be susceptible to an interpretation on the basis of an extension of this analysis to the experimental diffusion coefficients. In particular, if such an extension is made, the observed decrease in the experimental infinite-dilution coefficients of the hexane isomers in *n*-heptane, with the increase in branching or sphericity of the molecules, i.e.,



can possibly be related to the breaking of short-range order in the *n*-alkane structure due to the diffusion of the branched molecules.

The results obtained at a lower temperature (283 K) for the *n*-heptane + *n*-hexane and *n*-heptane + 2,3-dimethylbutane mixtures do not contradict this interpretation. The expected increase in correlation of molecular order in the pure *n*-heptane corresponds to a slight increase in the difference between the infinite-dilution diffusivities of *n*-hexane and 2,3-dimethylbutane. This is shown in Fig. 2, where the diffusion coefficients for these two systems at 283 and 298 K are presented as a function of composition. A satisfactory account of this statement can be made only when a wider range of temperatures is tested.

Results obtained in a different laboratory for the infinite dilution of *n*-octane and isooctane (2,2,4-trimethylpentane) in *n*-heptane [25] also show the decrease in the diffusion coefficients with branching.

A quantitative description of the present result can be attempted by means of the rough hard-spheres model. In a previous paper [4], this theory was applied to the systems *X* + *n*-heptane, where *X* = *n*-hexane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane, for which there were density and viscosity data available for the pure components [26, 28]. Table IV shows the values of the fluid hard-core volume,  $V_0$ , the hard-sphere diameter,  $\sigma$ , and the rotational coupling constant for viscosity,  $B$ , for those systems as well as for *n*-heptane + 2,3-dimethylbutane, for which the density was taken from Ref. 26 and the viscosity was estimated using a relation described in Ref. 27. The value of  $V_0$  for 2,3-dimethylbutane is consistent with the trend observed earlier [4], as it is smaller than for

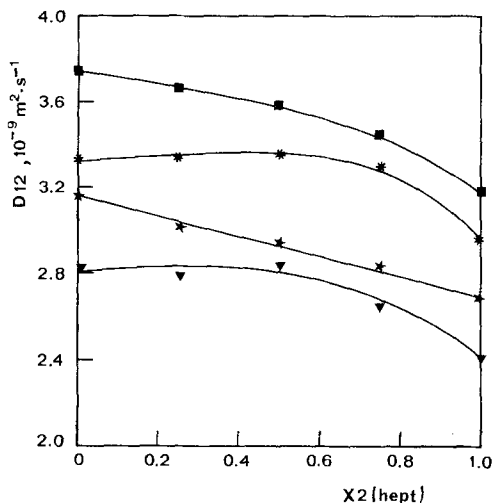


Fig. 2. The binary diffusion coefficient of *n*-hexane + *n*-heptane and 2,3-dimethylbutane + *n*-heptane at different temperatures. *n*-Hexane + *n*-heptane: (■)  $T=298$  K; (★)  $T=283$  K. 2,3-Dimethylpentane + *n*-heptane: (▲)  $T=298$  K; (▼)  $T=283$  K.

the 2,2 isomer. Also, the value obtained for  $B$  ( $1.11 \pm 0.03$ ) agrees with the average value for the other isomers ( $1.08 \pm 0.02$ ), showing that the collisional processes that determine viscosity in the liquid hexanes are essentially the same.

The values of the translational-rotational coupling constants for diffusion in the binary mixtures,  $A_{12}$ , are also shown in Table IV. The value of  $A_{12}$  is roughly the same for all the systems except 2,2-dimethylbutane + *n*-heptane. This may be attributed to the difficulty of the model in predicting a significant maximum in the composition dependence of the diffusion coefficients. Figure 3 compares the departures between experimental and theoretical values as a function of the composition of the mixtures. The shape of the deviations is roughly the same for all the systems. The departures amount to 17% for 2,3-dimethylbutane + *n*-heptane at 283 K. For all the other systems the theory can predict the experimental data to  $\pm 10\%$ .

Due to the unavailability of thermodynamic data on the mixtures, it has been assumed throughout these calculations [4] that the experimental diffusion coefficient is equal to the kinetic diffusion coefficient  $D_{12}^{\text{kin}}$ , within the uncertainty involved. Because the relation between these two coefficients is given by

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

**Table IV.** Rough Hard-Sphere Theory Volumes and Translational–Rotational Coupling Constants for Viscosity of the Pure Fluids,  $B$ , and for Diffusion in Binary Mixtures with  $n$ -Heptane,  $A_{12}$

Fluid	$10^6 V_0$ (m <sup>3</sup> · mol <sup>-1</sup> )	$10^8 \sigma$ (m)	$B$	Viscosity data From Ref. No.	$A_{12}$
<i>n</i> -Hexane	$82.13 \pm 0.08$	$5.78 \pm 0.01$	$1.10 \pm 0.02$	14	0.98
	$82.11 \pm 0.13$	$5.78 \pm 0.01$	$1.09 \pm 0.03$	15	
2-Methyl pentane	$82.27 \pm 0.15$	$5.78 \pm 0.01$	$1.08 \pm 0.04$	14	0.97 <sup>a</sup>
3-Methyl pentane	$81.60 \pm 0.14$	$5.77 \pm 0.01$	$1.06 \pm 0.03$	14	0.97
2,3-Dimethyl butane	$83.57 \pm 0.07$	$5.81 \pm 0.01$	$1.11 \pm 0.03$	16	0.98 <sup>b</sup>
2,2-Dimethyl butane	$85.25 \pm 0.03$	$5.85 \pm 0.00$	$1.08 \pm 0.08$	14	0.92
<i>n</i> -Heptane	$94.71 \pm 0.18$	$6.06 \pm 0.01$	$1.14 \pm 0.04$	15	0.96

<sup>a</sup> Estimated [4].

<sup>b</sup> Slightly temperature dependent (~1%).

where  $\gamma$  is the activity coefficient of component 1, this assumption is equivalent to the statement that the mixtures are ideal.

While for the system  $n$ -hexane +  $n$ -heptane this is certainly a good approximation, for the other systems its error increases with the degree of branching of the hexane isomer in the mixtures following the loss of CMO as described above. One should then expect that the deviations shown in Fig. 3 will be due partly to the thermodynamic factor in (1). On the other hand, the fact that even for the system  $n$ -hexane +  $n$ -heptane, this deviation, although smaller in magnitude, follows the same pattern with composition as the other systems is an indication that this is not the only effect and, perhaps, not the most important for the present discussion.

A possible justification of the failure of the van der Waals model in predicting the shape of the variation of the diffusion coefficients with composition can probably be found in the assumed linearity of the correction to the correlated motions in the dense phase previously proposed by Czworniak et al. [7], based on the molecular simulations of Alder et al. [29]. This correction  $C$  is a function of the packing fraction and the mass and size ratios and was assumed to be a linear function of composition.



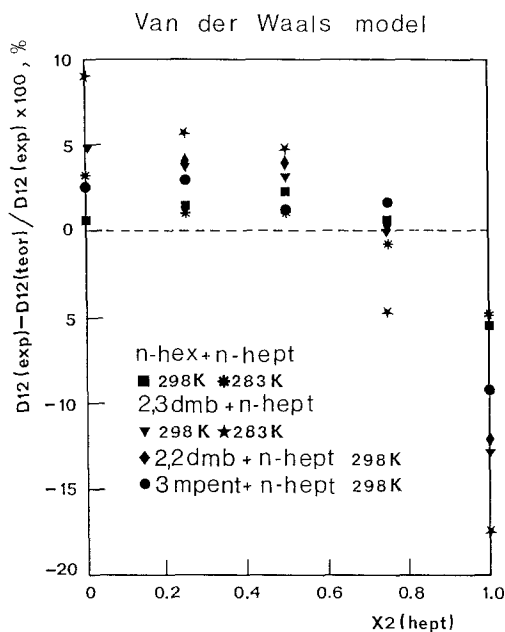


Fig. 3. Deviations between experimental and theoretical binary diffusion coefficients for the systems studied as a function of the molar fraction of *n*-heptane.

The present results seem to indicate that this is not an adequate relation. In fact the exact rough hard-sphere theory implies corrections to Enskog results for the entire concentration range for various size and mass ratios which are currently unavailable.

#### 4. CONCLUSIONS

A study of the influence of branching in the binary diffusion coefficients of *n*-hexane isomers in *n*-heptane around room temperature has been presented. The main features found, namely, the decrease in the diffusion coefficient with the increase in branching of the hexane isomers, seem to be interpretable on the basis of energetically favored segment interactions in the liquid mixtures.

It is also shown that at the present level of application, the approximate rough hard-sphere theory developed by Czwozniak et al. [7] for binary liquid mixtures cannot predict the composition dependence in these systems with an accuracy comparable with the experimental data. Effort is required in new theoretical developments and computer simulations.

Nevertheless, a more satisfactory interpretation of the present results will require some further study involving the measurement of the diffusivity of these systems at other temperatures and the calculation of their activity coefficients as a function of composition.

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