

## MOLECULAR AND THERMAL DIFFUSION COEFFICIENTS OF BINARY HYDROCARBON MIXTURE

*Alana Leahy-Dios, Abbas Firoozabadi, Yale University, New Haven, CT*

### ABSTRACT

The Ludwig-Soret effect (that is, thermal diffusion) describes the concentration gradient in a mixture under a temperature gradient. The effect is quantified by the Soret coefficient, which is in turn related to the molecular and thermal diffusion coefficients of a mixture. Thermal diffusion is important in a myriad of applications, such as in petroleum reservoirs, material sciences, oceanography, biological systems and chemical engineering.

There has been extensive theoretical and experimental work to model and measure thermal and molecular diffusion coefficients. However, there is no accurate predictive model for the explicit dependency of these coefficients on molecular size and shape. There are also a large number of important mixtures for which these coefficients have not been determined.

We have embarked on a major research effort to measure an extensive set of data on molecular and thermal diffusion coefficients of aromatic-alkane and alkane-alkane binary mixtures. A major objective of this work is to study the influence of molecular shape and size on the molecular and thermal diffusion coefficients of hydrocarbon binary mixtures. This study is intended to provide a framework for development of theoretical models.

Our experimental results indicate that molecular and thermal diffusion coefficients for aromatic-alkane binary mixtures have a different behavior than alkane-alkane binary mixtures, which suggests a strong dependency of these coefficients on molecular shape.

### I. INTRODUCTION

Molecular and thermal diffusion processes with a myriad of applications [1] are quantified by molecular and thermal diffusion coefficients,  $D$  and  $D^T$ , respectively. These coefficients are generally functions of temperature  $T$ , pressure  $P$  and composition  $\omega$  of the mixture. However, the dependency of  $D$  and  $D^T$  on  $T$ ,  $P$  and  $\omega$  has not been fully understood and determined either theoretically or experimentally. Molecular and thermal diffusion coefficients in a binary mixture relate to mass diffusion flux of component 1 according to

$$J_1 = -\rho(D\nabla\omega_1 + \omega_1(1-\omega_1)D^T\nabla T), \quad 1)$$

where  $\rho$  is the mixture mass density,  $\nabla\omega_1$  is the mass fraction gradient of component 1 and  $\nabla T$  is the temperature gradient. Based on thermodynamic stability analysis, when the thermal diffusion coefficient is positive, the component should segregate to the cold side in a binary mixture [2].

We measure  $D$  and  $D^T$  in n-decane-alkane and 1-methylnaphthalene-alkane binary mixtures. Our objectives are to: 1) study the  $D$  and  $D^T$  dependency on alkane chain size; and

2) investigate molecular shape effects on these coefficients. The molecules 1-methylnaphthalene and n-decane have nearly the same molecular weight but very different molecular shapes; by comparing results for these sets one may obtain a better understanding of molecular shape effects on  $D$  and  $D^T$  for this set of hydrocarbon mixtures.

Previous experimental work with hydrocarbons include determination of  $D$  for mixtures with alkane at infinite dilution [3] and studies on compositional effect on  $D$  [4] and  $D^T$  [5] for a limited range of alkane molecules. Some measurements for  $D^T$  have been performed for alkane-alkane mixtures [6,7] and monocyclic aromatic-alkane mixtures [8-11]. Unlike data in refs 3-11, our data cover a wide range of alkane molecular weight.

## II. MIXTURES STUDIED

The binary mixtures we have investigated are divided into two sets: SET 1 (MN- $nC_i$ ) comprises of binary mixtures of 1-methylnaphthalene and varying normal alkanes (n-pentane to n-hexadecane); SET 2 ( $nC_{10}$ - $nC_i$ ) contains the binary mixtures of n-decane and varying normal alkanes (n-pentane to n-eicosane). From here on, 1-methylnaphthalene will be referred to as MN, and normal alkanes as  $nC_i$  ( $i$  = number of carbon atoms). Measurements were performed at 25.0 °C, 1 atm and 50 wt% composition.

## III. EXPERIMENTAL TECHNIQUES

### A. Thermal Diffusion coefficient

We use the thermogravitational column technique to determine thermal diffusion coefficients. A schematic of the thermogravitational column is shown in Figure 1.

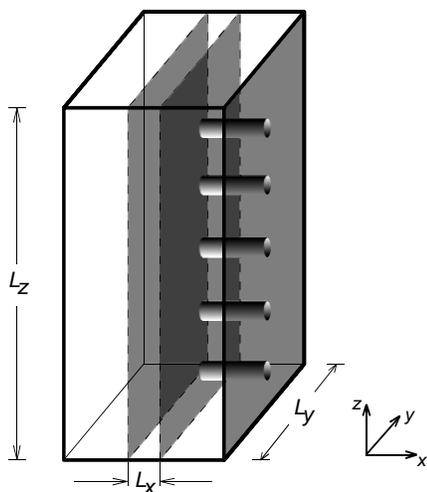


Figure 1: A sketch of the thermogravitational column, not to scale. The dimensions of the column are  $L_z = (46.7 \pm 0.1)$  cm,  $L_y = (4.7 \pm 0.1)$  cm and  $L_x = (1.60 \pm 0.02)$  mm.

In this technique, we determine  $D^T$  by measuring the compositional gradient of a mixture inside a column submitted to a linear temperature gradient. The following equation gives the thermal diffusion coefficients for component 1 in a binary mixture (see [12] for the simplifying assumptions and complete development of the working equation):

$$D^T = \frac{\rho_0 g \alpha L_x^4}{504 \mu \omega_1 (1 - \omega_1)} \frac{\Delta \omega_1}{\Delta z}. \quad (2)$$

In eq 2,  $\alpha$  is the thermal expansion coefficient  $\alpha = -(1/\rho_0)(\partial\rho/\partial T)$ ,  $g$  the gravitational acceleration,  $\mu$  the dynamic viscosity and  $(\Delta\omega_1/\Delta z)$  is the composition gradient of component 1 at steady-state. The separation in the column is independent of the temperature difference between the cold and hot plates.

## B. Molecular diffusion coefficient

We use the open-ended capillary tube technique [13] for molecular diffusion coefficient measurements. In this technique, we measure the composition change with time in small tubes at constant temperature. The mass balance of the heavier component of a binary mixture in the one-dimensional tube is written as:

$$\frac{\partial \omega_1}{\partial t} = D \frac{\partial^2 \omega_1}{\partial z^2}. \quad (3)$$

In eq 3,  $t$  is the time and  $z$  is the vertical distance (positive downwards). Local mass balance requires an extra (convective) term on the right hand side of eq 3. However, in this case the convective velocity inside the capillary tube is very small and this term is negligible. We Integrate eq 3 and apply boundary and initial conditions ( $\omega_1(z,0) = \omega_{1,0}$ ,  $\omega_1(0,t) = \omega_{1,\infty}$ ,  $\partial\omega_1/\partial z|_{z=L} = 0$ ) to obtain the working equation:

$$\frac{4L^2}{\pi^2} \ln \left( \frac{8(\omega_{1,0} - \omega_{1,\infty})}{\pi^2 (\langle \omega_1 \rangle - \omega_{1,\infty})} \right) = Dt. \quad (4)$$

where  $\omega_{1,0}$  is the initial mass fraction of component 1 and  $\omega_{1,\infty}$  is the mass fraction of the component 1 at the tube outlet (constant composition in the large bath),  $\langle \omega \rangle$  is the average composition and  $L$  is the tube length. [14] provides the complete development of the working equation and assumptions used. The slope of the left-hand side of eq 4 plotted vs. time provides  $D$  for the binary mixtures.

## IV. RESULTS AND DISCUSSION

Figure 2 depicts the essence of our  $D^T$  experiments for the two sets, where the data are plotted vs. the respective normalized alkane molecular weight (the ratio of n-alkane molecular weight to either nC<sub>10</sub> or MN molecular weight). In SET 1,  $D^T$  of MN is positive for all mixtures: MN behaves as the thermophobic species, segregating to the cold side. In SET 2,  $D^T$  for nC<sub>10</sub> is positive (nC<sub>10</sub> is the thermophobic species and segregates to the cold side) up to nC<sub>i</sub> = nC<sub>10</sub>; for nC<sub>i</sub> > nC<sub>10</sub>, nC<sub>10</sub> becomes the thermophilic species and segregates to the cold side.

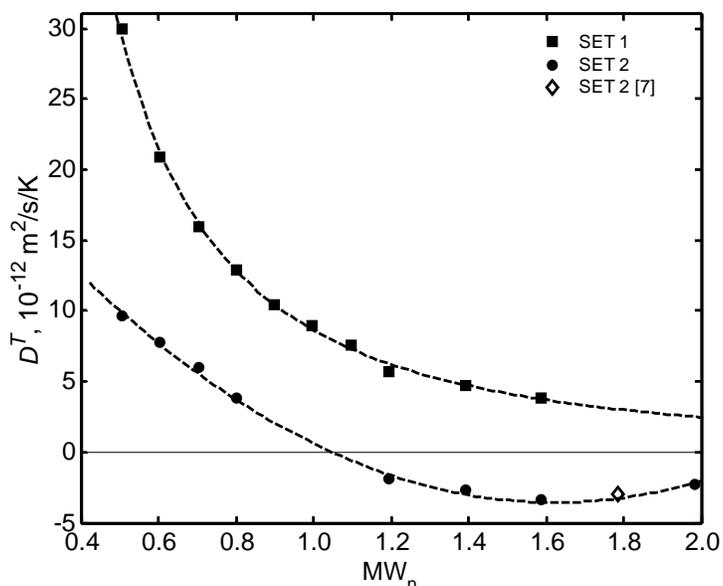


Figure 2:  $D^T$  vs. normalized alkane molecular weight ( $MW_{\text{alk}}/MW_{\text{MN}}$  for SET 1,  $MW_{\text{alk}}/MW_{\text{nC}_{10}}$  for SET 2). Dashed lines are fits to data. We show  $D^T$  for MN (SET 1) and  $\text{nC}_{10}$  (SET 2).

## B. Molecular Diffusion Coefficients

Figure 3 describes our results for  $D$  of both sets. Our results show that  $D$  for SET 2 is always greater than for SET 1. The binary mixtures that contain highly volatile components ( $\text{nC}_5$  to  $\text{nC}_7$ ) cannot be determined using open-ended capillary tube technique. We found data in the literature for  $\text{nC}_5$ - $\text{nC}_{10}$  [6] and  $\text{nC}_7$ - $\text{nC}_{10}$  [4] mixtures at 1 atm and close to  $25^\circ\text{C}$ , but different compositions. We estimated  $D$  values for these mixtures at 50 wt% by interpolation. For SET 2, we can obtain the self diffusion coefficient of  $\text{nC}_{10}$  from the best fit of the data. The predicted value of  $D_{\text{nC}_{10}\text{-nC}_{10}}$  from Figure 3 is in agreement with literature data [15-17].

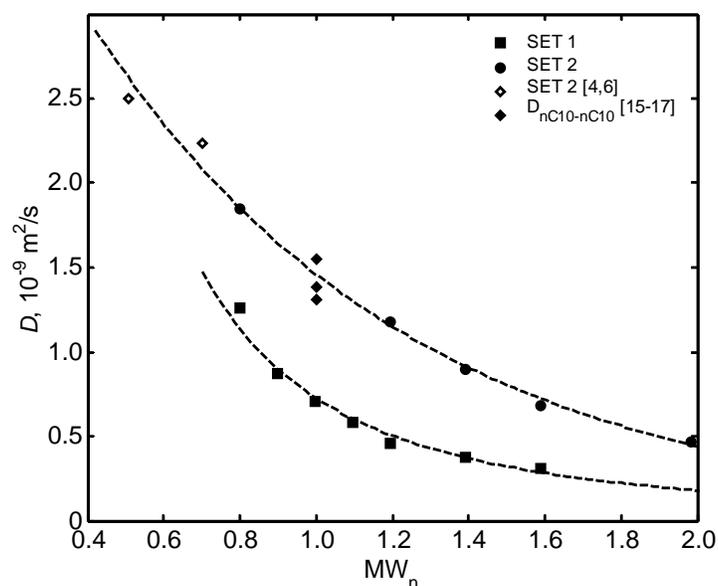


Figure 3:  $D$  vs. normalized alkane molecular weight ( $MW_n$ ) for SET 1 ( $\text{MN-nC}_i$ ) and SET 2 ( $\text{nC}_{10}\text{-nC}_i$ ).  $D$  for  $\text{nC}_{10}\text{-nC}_5$  and  $\text{nC}_{10}\text{-nC}_7$  are from refs 6 and 4, respectively.

### C. Effect of molecular shape

From Figure 2, we observe that  $D^T$  is generally greater for SET 1 than for SET 2 up to  $nC_i = nC_{14}$ . N-alkanes have similar molecular structure and therefore respond similarly to a temperature gradient, which explains the small  $D^T$  values in SET 2. On the other hand, MN has a very different molecular structure and shape compared to n-alkanes, which results in generally larger  $D^T$ s for SET 1. We expect that for SET 1,  $D^T$  will continue to decrease smoothly as the molecular weight of the alkane increases, until it reaches a positive asymptotic value. We expect a similar trend for other aromatic-n-alkane mixtures, provided the aromatic does not contain functional groups that change its chemical activity; this has been observed for benzene-alkane systems at 20°C. [9]. The behavior of  $D^T$  in SET 2 is very different:  $D^T$  decreases as  $MW_n$  increases, becomes zero at  $nC_i = nC_{10}$  as expected, displays a sign change and reaches a negative maximum value around  $nC_i = nC_{16}$  and decreases in magnitude for heavier alkane molecules; we expect it to reach a small negative asymptotic value for large alkane molecular weights.

In SET 1, the trend is monotonic, while in SET 2 there is non-monotonic behavior when results are plotted vs. the normalized molecular weight. Blanco *et al.* [7] have measured  $D^T$  for  $nC_{10}$ - $nC_{18}$  at 50 wt% each component and at 25°C. Our predicted value for  $nC_{10}$ - $nC_{18}$  fits very well to their data, and confirms the non-monotonic behavior of SET 2. These results suggest that molecular shape is an important factor in thermal diffusion coefficients.

The effect of molecular shape on molecular diffusion coefficient  $D$  also becomes evident when analyzing Figure 3; SETs 1 and 2 show different behaviors. Again, a trend very similar to that of SET 1 is observed in the benzene-alkane system [9].

### C. Effect of n-alkane chain length

When relating diffusion data to the alkane chain length, we hypothesize that there are two opposing factors that affect the diffusion coefficients, which we call the mobility of each individual component and the similarity between the components.

The mobility of each component is associated to Brownian motion and is a function of self diffusion coefficient and viscosity [18-20]. For n-alkanes, the longer the chain, the less mobile it is [21]. Component mobility increases  $D$  and  $D^T$ : more mobile molecules respond more strongly to temperature gradient. The similarity between the components relates to how differently each component will respond to a given force field, Physical properties such as boiling point, heat capacity, latent heat of vaporization and critical properties may relate to similarity between components. Similarity between components decreases  $D$  and  $D^T$ : alike molecules respond very similarly to temperature gradients and hardly separate.

To illustrate above idea, we examine SET 2 in Figure 2. From  $nC_5$  to  $nC_{10}$ , increasing the molecular weight of the n-alkane decreases  $nC_i$  mobility and increases similarity between  $nC_i$  and  $nC_{10}$ , both factor decrease  $D^T$ . As  $nC_i = nC_{10}$  (where similarity is maximum), similarity changes behavior and now decreases while mobility keeps decreasing. In this case, the two factors have competing effects; until  $nC_i = nC_{16}$  the similarity factor has a more important effect:  $D^T$  increases in magnitude since the molecules are becoming less similar, even though they are also becoming less mobile. For  $nC_i > nC_{16}$ , the mobility factor dominates and  $D^T$  decreases in magnitude, even though the molecules become less similar.

For SET 1, both effects are also present. Mobility decreases as alkane molecular weight decreases; however, we cannot determine at this point how the similarity factor between  $nC_i$  and MN changes; it seems to be increasing with increasing alkane molecular weight, therefore acting concurrently with mobility and decreasing  $D^T$ .

Figure 3 shows that molecular diffusion coefficients  $D$  in SET 2 are greater than those in SET 1. Analysis of benzene-alkane data [9] shows that  $D$  for all benzene- $nC_i$  mixtures is greater than for SET 1 and SET 2, even though  $nC_i$  molecules are more similar to  $nC_{10}$  than to MN and benzene. This indicates that the mobility factor dominates molecular diffusion, and the similarity factor is negligible. When we compare the self diffusion coefficient and viscosities of  $nC_{10}$ , benzene and MN at temperatures at or around 25°C [22-24], we find that benzene is the most mobile molecule, followed by  $nC_{10}$  and then MN. According to the mobility factor,  $D$  for the benzene-alkane mixtures should be greater than for SET 2, followed by SET 1. This is the behavior we observe experimentally.

## VII. CONCLUSIONS

In this work, we provide a systematic set of new measurements for two drastically different sets of binary hydrocarbon mixtures. In one set, comprised of binary mixtures of  $nC_{10}$  and n-alkanes ( $nC_5$  to  $nC_{20}$ ),  $D$  and  $D^T$  show a different trend when plotted vs. the n-alkane molecular weight. Thermal diffusion coefficients reveal a non-monotonic trend which may be due to the competing effect of molecular mobility and similarity. In another set, comprised of binary mixtures of 1-methylnaphthalene and n-alkanes ( $nC_5$  to  $nC_{16}$ ),  $D$  and  $D^T$  show a significant effect of molecular shape.

Interestingly, the plot of  $D^T$  vs. alkane molecular weight for the  $nC_{10}$ - $nC_i$  set provides a value of  $D^T \approx 0$  for pure  $nC_{10}$ . A similar plot for  $D$  of  $nC_{10}$ - $nC_i$  mixtures provides the self diffusion coefficient of  $nC_{10}$  in agreement with measured literature values.

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