Measurement of Thermodiffusion Coefficient in *n*-Alkane Binary Mixtures: Composition Dependence

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In this work, we have measured the thermodiffusion coefficient of different *n*-alkane binary mixtures at several concentrations using the thermogravitational technique. In particular, we have studied the *n*-dodecane/*n*-heptane system as a function of composition and other systems covering a large range of mass differences and concentration at 25 °C and 1 atm. The results show that for any concentration the thermodiffusion coefficient of *n*-alkane mixtures is proportional to the mass difference between the components and to the ratio of the thermal expansion coefficient and viscosity of the mixture. The obtained equation allows us to determine the infinite dilution values of the thermodiffusion coefficient. We compare these values with recent experimental results in dilute polymer solutions and analyze the Brenner theory of thermodiffusion. Finally, it is shown that the thermodiffusion coefficient depends linearly with the mass fraction, and it can be calculated from the viscosity and thermal expansion of the pure components.

I. Introduction

In an isothermal mixture, there is a transport of matter created by temperature gradients. This transport phenomenon is known as thermodiffusion or in particular for condensed systems as the Soret effect. According to nonequilibrium thermodynamics the mass flux of one component is given by

$$\vec{J} = -\rho D \nabla c - \rho D_{\mathrm{T}} c (1 - c) \nabla T \tag{1}$$

where ρ is the density; c is the mass fraction of the reference component; T is the temperature; D is the Fickian diffusion coefficient; and $D_{\rm T}$ is the thermodiffusion coefficient.

A survey of the literature over the past decade shows an increasing interest in thermodiffusion. However, there is still no microscopic theory to explain the thermodiffusion in liquids. According to Wiegand, the main features that determine the thermodiffusion in nonpolar fluids are the mass, moment of inertia, and size of the molecules as well as their interactions. Debuschewiz and Kölher² investigated the contribution of mass and moment of inertia differences by measurements in isotopic mixtures of benzene and cyclohexane. The influence of the molecular structure was analyzed by Polyakov et al.³ in mixtures of benzene with normal and branched n-alkanes, and Artola et al.4 determined by molecular dynamic simulations the chemical contribution to thermodiffusion. Finally, the influence of chain length in dilute polymer solution has been investigated by Stadelmaier and Köhler⁵ and rationalized by the theory developed by Würger.6

A number of studies have focused on the nonpolar *n*-alkane mixtures. These ideal mixtures have normal thermodiffusion behavior: the heavier component migrates always to the cold

side. Measurements of the thermodiffusion coefficient for different n-alkane mixtures have been recently performed using different techniques. Blanco et al.^{7,8} investigated the series nC_i/nC_{10} , nC_i/nC_{10} , nC_i/nC_{12} , and nC_i/nC_{18} at a molar fraction x=0.5 and nC_i/nC_{18} a mass fraction c=0.5. Leahy-Dios et al.^{9,10} studied the series nC_i/nC_{10} at decane mass fractions of c=0.25, 0.50, and 0.75. Yu Yan et al.¹¹ analyzed the series nC_i/nC_{12} at c=0.5. All these authors employed the thermogravitational method. Finally, Blanco et al.¹² analyzed the system nC_5/nC_{10} at different molar fractions and the series nC_i/nC_{10} at a mass fraction of c=0.5. They used both the thermogravitational and the thermodiffusion forced Rayleigh scattering techniques and obtained a good agreement between these two methods.

For equimolar mixtures it has been recently reported⁷ that for each of the above-mentioned series mass difference is the only parameter that determines the thermodiffusion coefficient. On the other hand, a quantitative correlation was found between the thermodiffusion coefficient, the mass difference, and the ratio of the thermal expansion coefficient and viscosity of the mixture.

In the present work, we shall extend this correlation to nonequimolar binary mixtures of n-alkanes and analyze the dependence of $D_{\rm T}$ with composition. Finally, we compare the obtained results with the Brenner¹³ theory of thermodiffusion and with the recent experimental results of Stadelmaier and Köhler⁵ for dilute polymer solutions.

II. Experimental Method

A. Equipment. The thermogravitational column used in this study is a conventional stainless steel concentric tube column, closed at both ends. It has been described in detail in earlier publications; for example, see ref 8 and references therein. The total length of the column is 0.49 m; the distance between the two sampling ports near the ends is 0.40 m; and the annular gap dimension is 1.2 mm. The temperature difference across the column is 10 °C with an average temperature of 25 °C.

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TABLE 1: Mixtures Considered, the Difference of Molecular Masses, and His Thermophysical Properties: Density (ρ) , Thermal Expansivity (α) , and Dynamic Viscosity (μ) at 25° C^a

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	mixture	ΔM 10^{-3} kg/mol	ρ kg/m³	$\frac{\alpha}{10^{-3}K^{-1}}$	μ 10^{-3} Pa s	$D_{\rm T}$ $10^{-12} {\rm m}^2/{\rm sK}$	$D_{\rm T}({\rm calcd})$ $10^{-12}{\rm m}^2/{\rm sK}$	$_{\%}^{\delta}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				$x_1 =$	0.80			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{10}-nC_7$	42.08	719.021	1.071	0.772	3.02	2.92	3.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{12}-nC_7$	70.13	736.409	1.005	1.118	3.69	3.59	2.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$nC_{15}-nC_8$	98.19	757.129	0.937	2.022	2.70	2.77	-2.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{16}-nC_7$	126.24	760.652	0.928	2.334	3.55	3.56	-0.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				$x_1 =$	0.40			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{10}-nC_7$	42.08	702.601			4.00	3.75	6.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{12}-nC_8$	56.11	721.000	1.060	0.807	3.39	3.31	2.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{17}-nC_{12}$	70.12	759.557	0.938	2.213	1.35	1.33	1.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{16}-nC_{10}$	84.17	747.768	0.960	1.520	2.37	2.39	-0.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$nC_{18}-nC_{11}$	98.20	757.000	0.933	2.220	1.89	1.85	1.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{18}-nC_7$	154.30	740.200	0.994	1.385	5.52	5.32	3.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				$x_1 =$	0.30			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{12}-nC_7$	70.13	706.600			5.30	5.38	-1.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{13}-nC_6$	98.18	700.261	1.142	0.610	7.71	7.49	2.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{14}-nC_6$	112.21	705.405	1.132	0.656	7.97	7.91	0.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{18}-nC_{10}$	112.22	748.413	0.964	1.584	2.83	2.83	0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$nC_{15}-nC_6$	126.24	705.000	1.115	0.707	8.16	8.10	0.7
$nC_{18}-nC_{7}$ 154.30 727.000 1.030 1.044 6.34 6.20 $x_{1}=0.20$ $rC_{12}-nC_{7}$ 70.13 698.661 1.159 0.530 5.82 5.87 $rC_{18}-nC_{12}$ 84.16 754.246 0.946 1.808 1.65 1.76 $rC_{18}-nC_{10}$ 112.22 741.925 0.985 1.311 3.07 3.16	$nC_{16}-nC_{6}$	140.27	708.000	1.110	0.745	8.37	8.15	2.6
$x_1 = 0.20$ $nC_{12} - nC_7$ 70.13 698.661 1.159 0.530 5.82 5.87 $- nC_{18} - nC_{12}$ 84.16 754.246 0.946 1.808 1.65 1.76 $- nC_{18} - nC_{10}$ 112.22 741.925 0.985 1.311 3.07 3.16	$nC_{18}-nC_{8}$	140.27	738.000	1.011	1.250	4.70	4.68	0.4
$nC_{12}-nC_{7}$ 70.13 698.661 1.159 0.530 5.82 5.87 - $nC_{18}-nC_{12}$ 84.16 754.246 0.946 1.808 1.65 1.76 - $nC_{18}-nC_{10}$ 112.22 741.925 0.985 1.311 3.07 3.16 -	$nC_{18}-nC_7$	154.30	727.000	1.030	1.044	6.34	6.20	2.2
$nC_{12}-nC_{7}$ 70.13 698.661 1.159 0.530 5.82 5.87 - $nC_{18}-nC_{12}$ 84.16 754.246 0.946 1.808 1.65 1.76 - $nC_{18}-nC_{10}$ 112.22 741.925 0.985 1.311 3.07 3.16 -				$x_1 =$	0.20			
$nC_{18}-nC_{10}$ 112.22 741.925 0.985 1.311 3.07 3.16 -	$nC_{12}-nC_7$	70.13	698.661	1.159	0.530	5.82	5.87	-0.9
	$nC_{18}-nC_{12}$	84.16	754.246	0.946	1.808	1.65	1.76	-6.5
$nC_{18}-nC_{7}$ 154.30 716.475 1.083 0.796 7.28 7.08	$nC_{18}-nC_{10}$	112.22	741.925	0.985	1.311	3.07	3.16	-3.1
	$nC_{18}-nC_7$	154.30	716.475	1.083	0.796	7.28	7.08	2.7

 a_{1} is the molar fraction of the heavier component; D_{T} is the measured thermodiffusion coefficient; and D_{T} (calcd) that calculated with eq 5.

In *n*-alkane mixtures, the heavier component always goes to the cold wall and thus concentrates at the bottom of the column. Thus, according to eq 1 $D_T > 0$ for this component. Further, in this article, we take the heavier component as the reference component, and it is denoted by subscript 1. The lighter component is denoted by subscript 2.

The theory of the thermogravitational columns, which was proposed by Furry–Jones–Onsager, $^{14-16}$ establishes a relation between the steady separation and the thermodiffusion coefficient $D_{\rm T}$ as follows

$$\Delta c_1 = \varphi c_1 c_2 \frac{\mu D_{\rm T}}{\rho \alpha} \tag{2}$$

where φ is a geometrical factor: $\varphi = (504L_z)/(gL_x^4)$, L_z being the column length, L_x the annular gap dimension, g the gravity acceleration, c_1 and c_2 the initial mass fractions of the heavier and lighter components, respectively, Δc_1 the steady separation between the column ends, α the thermal expansion coefficient, μ the dynamic viscosity; and ρ the density of the mixture.

To determine the separation Δc_1 , we measure the index of refraction of the two samples extracted from the sampling ports using a Pulfrich-type refractometer with a nominal accuracy of 5×10^{-6} . The composition of each sample is then determined from a calibration curve of refractive index as a function of concentration. Each experimental test is repeated three times for each mixture under consideration. To ensure that the stationary state is reached, we work at operation times that are considerably longer than the estimated relaxation time of the separation process. ¹⁶ The other required thermophysical properties, ρ , α , and μ , at 25 °C were also measured by us. A vibrating-quartz U-tube densimeter manufactured by Anton Paar (DMA)

5000) was used with an accuracy of 5×10^{-6} g/cm³ to measure the density ρ of the different mixtures at the mean temperature of 25 °C. By repeating the density measurements at different temperatures (24, 24.5, 25, 25.5, and 26 °C), the thermal expansion coefficient was determined. Dynamic viscosity μ was measured using the falling ball viscosimeter of Haake with an estimated error of $\pm 1\%$.

B. Studied Mixtures. All the products used in this study were purchased from Merck and Aldrich with purity higher than 99%. The mixtures have been prepared by introducing the less volatile component first, i.e., the alkane with higher molecular weight. Then the corresponding amount of second alkane is added. The concentrations of the binary mixtures are adjusted by weighing both components separately using a balance with an accuracy of 0.001 g. The sample volume needed to run an experiment is approximately 30 cm³.

We have prepared the mixtures that appear in Table 1 at the molar fractions of the heavier component $x_1 = 0.2$, $x_1 = 0.3$, $x_1 = 0.4$, and $x_1 = 0.8$. For each concentration, the mixtures cover a large range of mass difference to analyze the influence of this difference on the thermodiffusion coefficient. In this table, the values of the thermophysical properties α , ρ , and μ and the obtained values of D_T for each of the mixtures are displayed.

We have also studied the n-dodecane/n-heptane mixture at different molar fractions to determine the dependence of $D_{\rm T}$ with composition for a given mass difference. The measured values of the relevant thermophysical properties and $D_{\rm T}$ for each molar fraction appear in Table 2.

III. Discussion

A. Correlation of D_T with Other Physical Properties. In a previous work⁷ we found that for equimolar binary mixtures of n-alkanes the column separation is proportional to the mass

TABLE 2: Density (ρ), Thermal Expansion Coefficient (α), and Dynamic Viscosity (μ) for the System nC_{12}/nC_7 ($\Delta M = 70$) at 25 °C and Different Molar Fractions (x_1) of n-Dodecane^a

x_1	ρ (kg/m ³)	$\begin{matrix}\alpha\\(10^{-3}K^{-1})\end{matrix}$	μ (10 ⁻³ Pa s)	$D_{\rm T}$ $(10^{-12} {\rm m}^2/{\rm sK})$	$D_{\rm T}({\rm calcd})$ $(10^{-12}{\rm m^2/sK})$	δ %
0.10	689.767	1.202	0.475	6.34	6.20	2.2
0.20	698.661	1.158	0.530	5.82	5.87	-0.9
0.30	706.600	1.124	0.611	5.30	5.39	-1.7
0.37	711.000	1.102	0.682	5.08	5.00	1.6
0.50	720.378	1.066	0.807	4.50	4.49	0.2
0.70	731.471	1.023	1.004	3.86	3.89	-0.7
0.80	736.409	1.004	1.118	3.69	3.59	2.7
0.90	740.949	0.990	1.234	3.35	3.31	1.1

 $^{^{}a}D_{T}$ is the measured thermodiffusion coefficient, and D_{T} (calcd) is that calculated from eq 5.

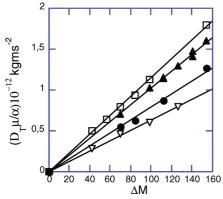


Figure 1. $\mathcal{D}_T \mu / \alpha \mathcal{D}_T = \mathcal{D}_T c_1 c_2$ ($\mathcal{D}_T = \mathcal{D}_T c_1 c_2$) values of the systems in Table 1 as a function of the molecular weight difference, $\Delta M = M_1 - M_2$, for the molar fractions: \bullet , $x_1 = 0.20$; \blacktriangle , $x_1 = 0.30$; \Box , $x_1 = 0.40$; ∇ , $x_1 = 0.80$. Solid straight lines are a fit of experimental data.

difference, $\Delta M = M_1 - M_2$, between the components of the mixture. According to eq 2, that means that this proportionality holds for the quantity $(\mathcal{D}_T \mu)/(\alpha)$, where \mathcal{D}_T is the coefficient of the thermal gradient in eq 1 $(\mathcal{D}_T = D_T c_1 c_2)$. In what follows and based on column separation data, we shall show that this proportionality can be extended to nonequimolar mixtures.

In Figure 1, the values of $(\mathcal{D}_T \mu)/(\alpha)$ are plotted as a function of ΔM for the *n*-alkane mixtures in Table 1 for molar fractions $x_1 = 0.2, 0.3, 0.4$, and 0.8. As shown in the figure, these values for each composition lie on a straight line through the origin. Therefore, one can tentatively write the following correlation

$$\frac{\mathcal{D}_{\mathrm{T}}\mu}{\alpha} = k(x_1)\Delta M \tag{3}$$

where $k(x_1)$ only depends on the molar fraction. Being independent of ΔM , it can be conveniently determined from experimental data of $(\mathcal{O}_T \mu)/(\alpha)$ at different molar fraction for a reference n-alkane binary system. With regard to this, we have taken the n-dodecane/n-heptane system, where the mass difference between the components is $\Delta M = 0.070$ kg/mol. The thermophysical properties at the different concentrations considered are shown in Table 2.

In Figure 2, $(\mathcal{D}_T \mu)/(\alpha)$ for this system versus the concentration is shown. As can be seen, the data fit to a parabolic line. Then, $k(x_1)$ is given by the equation of the fitted line divided by the mass difference. In this way, the following is obtained

$$k(x_1) = (5.34x_1 - 7.00x_1^2 + 1.65x_1^3)10^{-11}$$
 (4)

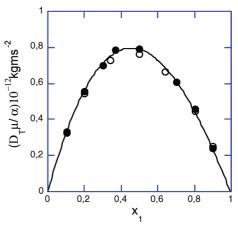


Figure 2. $\mathcal{D}_T \mu / \alpha$ values as a function of the molar fraction of the heavier component x_1 . \bullet , n-dodecane/n-heptane. Solid line is a fit of experimental data. For comparison, we have shown the values for n-decane/n-pentane from ref 12 (O).

For $x_1 = 0.5$, $k(x_1) = 1.15 \times 10^{-11}$ m s⁻², and this is in agreement with the value obtained for equimolar mixtures in a previous work.⁷

In Figure 2, the data of $(\mathcal{O}_T \mu)/(\alpha)$ for the *n*-decane/*n*-pentane system at several concentrations, taken from ref 12, are also shown. The mass difference between the components is $\Delta M = 0.070$ kg/mol, which is the same as that for the *n*-heptane/*n*-dodecane system. Thus, according to eq 3, $(\mathcal{O}_T \mu)/(\alpha)$ is the same for each concentration in both systems. As shown in Figure 2, the experimental points for *n*-decane/*n*-pentane lie on the curve corresponding to *n*-dodecane/*n*-heptane, which is in agreement with eq 3.

According to the results obtained above, we can use for \mathcal{D}_T the following correlation

$$\mathcal{D}_{\mathrm{T}} = k(x_1)(M_1 - M_2)\frac{\alpha}{\mu} \tag{5}$$

where $k(x_1)$ is given by eq 4. To confirm the validity of this correlation, we have determined the values of $D_T = \mathcal{D}_T/c_1c_2$ from eq 5 for the mixtures given in Tables 1 and 2. As shown in these tables, the agreement between the obtained values and the experimental ones is within the error of the measurements.

As an additional test of eq 5 we have used the experimental $D_{\rm T}$ values for the mixtures $n{\rm C}_{10}/n{\rm C}_i$ (i=5,6,7,15,16,17,18, and 20) at the mass fraction $c_1=0.5$ as reported in ref 12. We have also used $D_{\rm T}$ values for the mixtures $n{\rm C}_{18}/n{\rm C}_i$ (i=5,6,7,8,9,10,11,12, and 13) and $n{\rm C}_{12}/n{\rm C}_i$ (i=5,6,7,8,9,17, and 18) at $c_1=0.5$ from ref 8 and 11, respectively. In Figure 3 the values of $D_{\rm T}$ determined using eq 5 are plotted against the

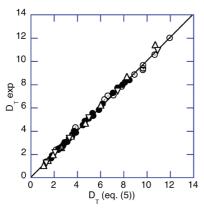


Figure 3. Comparison of experimental and calculated thermodiffusion coefficients of the mixtures from eq 5: \blacksquare , in this work; \triangle , in ref 12; \bigcirc , in ref 7; ∇ , in ref 11. Solid straight line is a fit of data.

experimental ones for each mixture. As seen here, all the data lie on a straight line through the origin with slope unity. Therefore, we can conclude that eq 5 helps in determining the accurate values of the thermodiffusion coefficient for any *n*-alkane binary mixture from viscosity and thermal expansion data of the mixture.

B. Dilute Solutions. For the purpose of comparison with recent theories^{13–17} and experimental results,⁵ it is convenient to determine D_T in the dilute region. Taking into account that for a dilute solution of the heavier component as solute $(x_1 \rightarrow 0)$ is

$$c_1 c_2 \approx c_1$$
 and $c_1 \approx \frac{M_1}{M_2} x_1$

and further $k(x_1)$ reduces to

$$k(x_1) = 5.34 \times 10^{-11} x_1$$

we obtain from eq 5 for the infinite dilution value of $D_{\rm T}$

$$D_{\rm T}(x_1 \to 0) = 5.34 \times 10^{-11} \left(\frac{\alpha_2}{\mu_2}\right) M_2 \left(1 - \frac{M_2}{M_1}\right)$$
 (6)

where M_2 , α_2 , and μ_2 are the molar mass, the thermal expansion coefficient, and the viscosity of the lighter component (the solvent). M_1 is the molar mass of the heavier component (the solute), and $D_{\rm T}$ is the thermodiffusion coefficient of this component. Thus, $M_1 > M_2$ and $D_{\rm T} > 0$.

As can be seen, $D_{\rm T}$ depends on the ratio α_2/μ_2 . This dependence is predicted by the two theories of thermodiffusion of Semenov and Shimpf¹⁷ and Brenner.¹³ The dependence of $D_{\rm T}$ with inverse viscosity of the solvent has also been experimentally confirmed by Hartung et al.¹⁸ for dilute polymer solutions.

Equation 6 can be written in the form

$$D_{\rm T}(x_1 \to 0) = \bar{D}_{\rm T} \left(1 - \frac{M_2}{M_1}\right) \text{ where } \bar{D}_{\rm T} = 5.34 \times 10^{-11}$$

$$\left(\frac{\alpha_2}{\mu_2}\right) M_2 \quad (7)$$

which shows that $D_{\rm T}$ increases with the molecular mass of solute

and extrapolating to large M_1 reaches for $M_1 \gg M_2$ a solute molar mass independent plateau $D^-_{\rm T}$. The deviation of $D_{\rm T}$ from the asymptotic plateau shows an M_1^{-1} dependence, and the plateau value is inversely proportional to the solvent viscosity. A similar behavior has been observed in a recent paper of Stadelmaier and Köhler⁵ for dilute polymer and n-alkane solutions in different solvents. The theory developed by Würger⁶ explains this dependence of $D_{\rm T}$ with the molecular mass of solute. Moreover, if we consider for instance the dilute mixtures of n-alkanes in n-pentane as solvent, the plateau value according to eq 7, $D^-_{\rm T} = 0.62 \times 10^{-14}/\mu_2$, in agreement with the expression proposed by Stadelmaier and Köhler⁵ for dilute polymer solutions.

As the Semenov and Shimpf theory¹⁷ includes parameters that are difficult to assign to *n*-alkane mixtures, in what follows we will compare our results to the theory of thermal diffusion developed by Brenner.¹³ According to this theory, the thermodiffusion coefficient in the dilute region for solute large molecules compared with those of the solvent is given by

$$D_{\rm T} = \lambda \alpha_2 D_{\rm s} \tag{8}$$

where D_s is the self-diffusion coefficient of the solvent and λ is an unknown nondimensional parameter of O(1) independent of the nature of solute that becomes unity for ideal mixtures.

To test the validity of eq 7, we consider the dilute solutions of *n*-decane and *n*-octadecane in the solvent *n*-pentane. The needed thermophysical properties of *n*-pentane are $D_{\rm s}=5.5\times 10^{-9}~{\rm m}^2/{\rm s}$ (ref 19) and $\mu_2=0.224\times 10^{-3}$ Pa s. Thus, $\mu_2D_{\rm s}=1.23\times 10^{-12}~{\rm kg~m/s}^2$, and comparing eqs 6 and 8, we obtain for λ

$$\lambda = 43.4 M_2 \left(1 - \frac{M_2}{M_1} \right) \tag{9}$$

which depends on the molecular mass of solute M_1 in disagreement with Brenner's model. For the solute, n-decane is $\lambda = 1.54$ and n-octadecane is $\lambda = 2.24$, and thus λ is of O(1) although it differs from unity despite the ideality of the mixtures. Therefore, the Brenner formulation with $\lambda = 1$ can be used for a rough estimation of $D_{\rm T}$. Similar results have been recently obtained by Hartung et al. 18 for dilute mixtures of polystyrene in different solvents.

Finally, we shall determine the limiting value of D_T for $x_1 \rightarrow 1$ $(x_2 \rightarrow 0)$, i.e., when the heavier component is the solvent. We have for $D_T(x_2 \rightarrow 0)$ from eqs 4 and 5

$$D_{\rm T}(x_2 \to 0) = 3.71 \times 10^{-11} \left(\frac{\alpha_1}{\mu_1}\right) M_1 \left(\frac{M_1}{M_2} - 1\right)$$
 (10)

where α_1 and μ_1 are the thermal expansion and viscosity of the solvent.

C. Dependence of $D_{\rm T}$ with Concentration. In Figure 4 the values of $D_{\rm T}$ plotted against the mass fraction of the lighter component, c_2 , for the n-dodecane/n-heptane (Table 1) and n-decane/n-pentane (ref 10) systems are shown. As can be seen, $D_{\rm T}$ data for each system fit to a straight line of positive slope which shows that $D_{\rm T}$ increases linearly with the mass fraction of the lighter component. Therefore, we can write for $D_{\rm T}$ the following linear equation

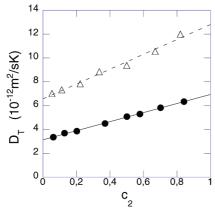


Figure 4. Thermodiffusion coefficient as a function of the mass fraction, c_2 , of the lighter component. \bullet , n-dodecane/n-heptane; Δ , *n*-decane/*n*-pentane.

$$D_{\rm T} = c_1 D_{\rm T}(c_2 \to 0) + c_2 D_{\rm T}(c_1 \to 0) \tag{11}$$

where $D_{\rm T}(c_1 \rightarrow 0)$ and $D_{\rm T}(c_2 \rightarrow 0)$ are the limiting values of $D_{\rm T}$ for $c_1 \rightarrow 0$ and $c_2 \rightarrow 0$, respectively. According to this equation, the limiting values of $D_{\rm T}$ determine $D_{\rm T}$ in all the concentration

By using eq 6 and eq 10, one can calculate the limiting $D_{\rm T}$ values from viscosity and thermal expansion coefficient data of the pure components. These data measured by us for all liquid *n*-alkanes appear in Table 3. Then, eq 11 allows us to predict $D_{\rm T}$ for the full range of concentrations.

We have checked the validity of eqs 6, 10, and 11 for all the mixtures of *n*-alkanes in the references quoted above. The results show that these equations allow us to predict D_T with the same accuracy as eq 5. For instance, these equations reproduce the $D_{\rm T}$ data for all the mixtures in ref 7 and Table 1 with deviations smaller than 5%. As another example, in Figure 5, $D_{\rm T}$ data for the mixtures of *n*-octadecane with *n*-heptane, *n*-decane, and n-pentane versus the mass fraction of the lighter component are plotted. The solutions of *n*-octadecane/*n*-pentane present the higher mass difference of n-alkanes studied. The data for equimolar and equimass mixtures are taken from ref 8 and for other concentrations from Table 1. We have also represented the limiting values for $c_1 \rightarrow 0$. The other limiting value when $c_2 \rightarrow 0$ cannot be calculated because the *n*-octadecane is solid at 25 °C. As can be seen, the experimental points and the calculated ones for $D_T(c_1 \rightarrow 0)$ are in a straight line. It can also be observed that the increase of $D_{\rm T}$ with the concentration of the lighter

TABLE 3: Molar Masses (M), Density (ρ) , Thermal Expansion Coefficient (α), and Dynamic Viscosity (μ) at 25°C for the *n*-Alkanes Used in This Work

solvent	M (10 ⁻³ kg/mol)	ρ (kg/m ³)	$\alpha (10^{-3} \text{K}^{-1})$	$\mu (10^{-3} \text{Pa s})$
pentane	72.15	621.77	1.61	0.224
hexane	86.18	655.12	1.38	0.300
heptane	100.20	679.78	1.24	0.387
octane	114.23	698.76	1.16	0.508
nonane	128.25	713.96	1.09	0.665
decane	142.28	726.09	1.04	0.838
undecane	156.30	736.74	1.00	1.098
dodecane	170.34	745.15	0.971	1.383
tridecane	184.36	752.89	0.951	1.724
tetradecane	198.39	759.34	0.930	2.128
pentadecane	212.42	765.36	0.920	2.570
hexadecane	226.45	770.21	0.910	3.032
heptadecane	240.26	774.52	0.905	3.690

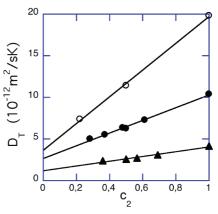


Figure 5. Thermodiffusion coefficient as a function of the mass fraction, c_2 , of the lighter component. \bigcirc , *n*-octadecane/*n*-pentane; \bigcirc , n-octadecane/n-heptane; \triangle , n-octadecane/n-decane.

component is enhanced with increasing mass difference between the two alkanes. This behavior has also been observed for Lennard-Jones mixtures by molecular dynamics simulation.²⁰

IV. Conclusions

In this study, we have measured the thermodiffusion coefficient of several n-alkane mixtures at different concentrations by the thermogravitational method. We have found a linear universal correlation between the thermodiffusion coefficient, the mass difference, and the ratio of the thermal expansion coefficient and viscosity. This correlation helps to determine quantitatively the thermodiffusion coefficient of any binary mixture of *n*-alkanes. In particular, the infinite dilution values of $D_{\rm T}$ can be calculated.

We have shown that in dilute solutions of *n*-alkanes D_T increases with the molar mass of solute reaching a molar mass independent plateau, in accordance with recent studies for dilute polymer solutions. Moreover, we have checked the Brenner theory of thermodiffusion.

Finally, we have found that the thermodiffusion coefficient in *n*-alkane mixtures depends linearly on the mass fraction. This result allows us to determine accurate D_T values from viscosity and thermal expansion coefficient of the pure components.

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