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Determination of Molecular Diffusion Coefficient in *n*-Alkane Binary ² Mixtures: Empirical Correlations

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ABSTRACT: In this work we have measured the molecular 7

diffusion coefficient of the *n*-alkane binary series $nC_i - nC_{6i} - nC_{6i}$ 8

nC10, and nCi-nC12 at 298 K and 1 atm and a mass fraction of 9

0.5 by using the so-called sliding symmetric tubes technique. 10

The results show that the diffusion coefficient at this 11

concentration is proportional to the inverse viscosity of the 12

mixture. In addition, we have also measured the diffusion 13

coefficient of the systems nC_{12} - nC_{6} , nC_{12} - nC_{7} , and nC_{12} - nC_{8} as a function of concentration. From the data obtained, it is shown 14

- that the diffusion coefficient of the n-alkane binary mixtures at any concentration can be calculated from the molecular weight of 15
- the components and the dynamic viscosity of the corresponding mixture at 50% mass fraction. 16

I. INTRODUCTION

17 A concentration gradient within a mixture results in a mass 18 transport of its components from the zones of a higher 19 concentration to those of a lower concentration. This pheno-20 menon, known as molecular diffusion, has generated great 21 interest since its discovery in the nineteenth century when, first 22 in gases and later on in liquids, it was studied with the aim of 23 understanding the atom's behavior.

It was in 1855 when Fick¹ established the first quantitative 24 25 relation for the molecular diffusion phenomenon, known 26 nowadays as Fick's law. Since then, interest in this transport 27 property has increased, discovering a great number of fields in 28 which the molecular diffusion coefficient has a huge influence, 29 such as medicine or phisiology.²

As a consequence of this interest, there have appeared a 30 31 great number of apparatus designed for the determination of 32 the molecular diffusion coefficient. There are, for example, 33 techniques that employ the principle of Taylor dispersion³ or 34 other techniques such as open ended capillary (OEC)⁴ or 35 thermal diffusion forced Rayleigh scattering (TDFRS)⁵ 36 developed for the study of the molecular diffusion coefficient 37 in liquid mixtures. The different techniques used for the deter-38 mination of the molecular diffusion coefficient can be found 39 elsewhere.^{2,6–9}

Some of these techniques, such as the OEC, have already 40 41 been satisfactorily used in several studies earlier.^{4,10} With the 42 aim of correcting some of the limitations of this technique, the 43 sliding symmetric tubes (SST) technique has been developed. 44 This new technique takes out perturbations that appeared in 45 the OEC technique, especially in aspects such as evaporations 46 or manipulation of the apparatus, reducing, at the same time, 47 the liquid quantity needed to carry out a measurement. In this 48 work a complete description of the SST technique will be done, 49 including the improvements obtained compared with the OEC

technique, and the validation process used to validate this new 50 technique.

On the other hand, nowadays, there exist several models 52 developed for the estimation of the molecular diffusion 53 coefficient.^{11,12} In order to check the validity of these models, 54 it is necessary to compare the theoretical values obtained with 55 the experimental ones. On some occasions, the procedure that 56 checks these models requires a huge number of experimental 57 values, which, at the same time, requires a great experimental 58 effort. In this work, a new correlation, which is capable of 59 predicting the molecular diffusion coefficient in normal alkane 60 binary mixtures, is presented. The use of this correlation may 61 help in the development of new theories or could be useful in 62 verifying the existing ones.

This article is organized as follows: In section II, the SST 64 technique is presented, and a complete description of the 65 experimental installation and its analytical resolution is done. In 66 this section, the process used to validate the technique is also 67 included. In section III, the results obtained in the measure- 68 ment of the molecular diffusion coefficient in several normal 69 alkane mixtures are presented, to continue with the discussion 70 and the development of new correlations for the prediction of 71 the molecular diffusion coefficient (D_{12}) in normal alkane 72 mixtures. In section IV, the conclusions obtained are based on 73 the study carried out in this work. 74

II. SST TECHNIQUE

A. SST Technique Description. The SST technique 75 consists of several sets of two identical vertical tubes. Each 76 set has two positions: "faced tubes" (Figure 1a), in which the 77

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Figure 1. (a) Scheme of the sets of the SST technique on "faced tubes" configuration. (b) Scheme of the sets of the SST technique on "separated tubes" configuration. (c) Scheme of the SST sets (2) inside the water bath (3) in both their configurations: "faced tubes" position (left) and "separated tubes" position (right) and the screws (1) used to make the tubes slide. (d) Scheme of SST technique. $w^{top}(t)$ and $w^{bot}(t)$ are the mass fractions of component *i* in the top and bottom recipient, respectively.

78 mass transfer between both tubes is permitted, and "separated 79 tubes" (Figure 1b). In this position, the content of the tubes is 80 isolated. At the beginning of an experiment, the studied mixture 81 with a slight difference of mass fraction of its components is 82 introduced in each of the tubes. The mixture with a higher mass 83 fraction of the denser component is introduced in the bottom 84 tube, and the upper tube is filled with the mixture with a less 85 concentration of the denser component so that the convective 86 instability is avoided.

The SST technique introduces some improvements 87 88 compared with the OEC technique on which it is based. For 89 example, since the mixture is contained inside closed tubes, 90 evaporations are eliminated, which gives the advantage of using 91 this technique with volatile mixtures without reducing its 92 efficiency. Another fact that has been improved has been the 93 mixture quantity needed to carry out an essay. The OEC ⁹⁴ technique requires a huge quantity of mixture (400 cm³ 95 approximately). This quantity is highly reduced in the SST 96 technique, as it only needs around 100 cm³ of mixture in each 97 experiment. One more improvement has been done related to 98 the setup handling. In the OEC technique, whenever it is 99 needed to analyze the experiment evolution, it is necessary to 100 manipulate the setup. This fact affects the results of the 101 experiment, which are highly influenced by the experimenter's 102 expertise. However, in the SST technique, thanks to its design, 103 all of these influences have been eliminated.

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B. Analytical Solution. Assuming Fick's second law in one 104 dimension (*z*: vertical direction), the following can be written: 105

$$\frac{\partial w}{\partial t} = D_{12} \frac{\partial^2 w}{\partial z^2} \tag{1}$$

where D_{12} is the molecular diffusion coefficient, which is 106 considered constant for small mass fraction (*w*) changes. The 107 formulation can be implemented as can be seen in Figure 1d 108 considering the following boundary conditions: 109

$$w(z, 0) = \begin{cases} w^{\text{bot}} & 0 \le z < L \\ w^{\text{top}} & L < z \le 2L \end{cases}$$
(2)

$$\frac{\partial w(z, t)}{\partial t} = 0 \text{ at } z = 0, \ 2L \text{ and } t > 0$$
(3)

where w^{bot} and w^{top} are the mass fractions of the bottom and 110 upper tube, respectively, and L is the tube length. Solving 111 eqs 1–3, we have 112

$$w(z, t) = \frac{w^{\text{top}} + w^{\text{bot}}}{2} - \frac{2(w^{\text{top}} - w^{\text{bot}})}{\pi}$$
$$\sum_{n=0}^{\infty} \frac{(-1)^n e^{\phi} \cos\left(\frac{2n+1}{2}\pi \frac{z}{L}\right)}{2n+1}$$
(4)

where $\varphi = -((2n + 1)/2)^2(\pi/L)^2D_{12}t)$. Therefore, at the 113 middle point between both the tubes, we have 114

$$w(L, t) = \frac{w^{\text{top}} + w^{\text{bot}}}{2}$$
(5)

The change of mass fraction in each tube in function of time 115 can be obtained using the following equations: 116

$$\overline{w^{\text{top}}(t)} = \frac{1}{L} \int_{L}^{2L} w(z, t) dz$$
$$= \frac{w^{\text{top}} + w^{\text{bot}}}{2} + \frac{4(w^{\text{top}} - w^{\text{bot}})}{\pi^2}$$
$$\sum_{n=0}^{\infty} \frac{e^{\varphi}}{(2n+1)^2}$$
(6)

$$\overline{w^{\text{bot}}(t)} = \frac{1}{L} \int_{0}^{L} w(z, t) dz$$
$$= \frac{w^{\text{top}} + w^{\text{bot}}}{2} - \frac{4(w^{\text{top}} - w^{\text{bot}})}{\pi^{2}}$$
$$\sum_{n=0}^{\infty} \frac{e^{\varphi}}{(2n+1)^{2}}$$
(7)

where $\overline{w^{\text{top}}}$ and $\overline{w^{\text{bot}}}$ are the mean mass fractions in the upper 117 and bottom tube, respectively. The solution of the inverse 118 problem posed by eqs 6 and 7 to obtain the molecular diffusion 119 coefficient (D_{12}) is solved by the least-squares method using 120 *Matlab* software. Solving expressions 6 and 7 when n = 0, an 121 initial guess of the molecular diffusion coefficient D_{12} is 122 obtained. This initial value is then used for obtaining the D_{12} 123 coefficient iterating the eqs 10 times and using terms on the 124 summation up to n = 1000. The more experimental points 125 used, the more accurate the estimated value of the molecular 126

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127 diffusion coefficient. Typically up to 11 points are used in each 128 experiment. This tactic allows the use of experimental points 129 from the very beginning of the experiment, which does not 130 happen in other similar techniques that require some initial 131 experimental time before beginning the analysis of experimental 132 data.^{3,8}

C. Equipment and Procedure. We have used the SST 133 134 equipment designed and constructed in Mondragon Goi Eskola 135 Politeknikoa and described elsewhere. $^{13-15}$ The two tubes with 136 which each set of the device is provided have the same dimen-137 sions (length of 60 ± 0.01 mm and diameter of 9 ± 0.01 mm). The experimental procedure starts with the preparation 138 139 of two mixtures of 50 cm^3 with a mass fraction difference $140 (\pm 4-6 \text{ wt }\%)$ so that the mean concentration of both mixtures 141 corresponds with the one of the mixture to be studied. The 142 tubes of several sets (typically 10) in their "separated tubes" 143 position are filled with the mixtures, next introducing the sets in 144 the water bath (Figure 1d) so that the mixture obtains the 145 working temperature (T = 298 K). The temperature of the 146 water in this bath is controlled by a thermostatic bath, which 147 has a temperature control of 0.1 K. In order to make sure that 148 the studied mixture is in the working temperature, the sets in 149 their "separated tubes" configuration are introduced in the bath 150 no less than 48 h before the beginning of the experiment.

Once the mixture has reached the working temperature, 152 all the sets in the bath are changed to their "faced tubes" 153 configuration, starting the diffusion process in this manner. 154 With the aim of making this transition, the bath has some 155 external screws (Figure 1c) that make sliding of the tubes 156 possible in a controlled way.

In determined time intervals, the position of the sets is changed one by one using the screws back to the "separated two position." The time intervals in which the set's positions are changed are between 6, 12, or 24 h, depending on the speed that which sensitive concentration changes occur in the tubes. After stopping the mass transfer process between the tubes, the sets are extracted from the bath, and the concentration in each the of them is analyzed. This allows obtaining the concentration the tubes in function of time.

The SST technique was validated^{13,14} using five binary mixtures: the three binary mixtures composed of pairwise combinations of tetrahydronaphtalene, normal dodecane, and isobutylbenzene at 298 K and 50 wt % of each component used no in a benchmark test¹⁶ to compare various experimental techniques and the binary mixtures: water—ethanol at 298 K and 60.88 wt % water and toluene-n hexane at 298 K and 51.67 wt % toluene, which have been widely studied in the literature.^{17–20} The experimental test was repeated at least twice. The re-

174 The experimental test was repeated at least twice. The re-175 producibility of the experimental results of the SST technique is 176 within 3% of deviation. In general, the differences with pub-177 lished data are, on an average, below 3%.

The determination of the mass fraction of a mixture is respectively an arrival structure is a mixture is to determine molecular diffusion coefficients. In binary mixtures, the mass fraction is related to one physical property respectively in this experimental study). An respectively in this experimental study). An respectively and a mixture of the density in this experimental study). An respectively and a study of the density of the mixture. Since we are working with small respectively mass fraction differences, it can be supposed that

$$o = aw_i \tag{8}$$

186 where ρ is the density of the mixture, w_i is the mass fraction of 187 component i in the binary mixture, and *a* is a constant

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Table 1. Values of Viscosity (μ) and Molecular Diffusion Coefficient (D_{12}) for the nC₆-nC_i, nC₁₀-nC_i, and nC₁₂-nC_i Series at 50 wt % and 298 K^{*a*}

system	μ mPa s	$D_{12} \ 10^{-9} \ \mathrm{m^2 \ s^{-1}}$	$(\overline{D_{12}})_{cc} 10^{-9} \text{ m}^2 \text{ s}^{-1}$	δ (%)					
set 1: nC _i -nC ₆									
$nC_{10}-nC_{6}$	0.4704	2.53	2.51	0.8					
$nC_{11}-nC_6$	0.5312	2.27	2.22	2.1					
nC_{12} - nC_{6}	0.5581	2.09	2.11	-1.2					
nC ₁₃ -nC ₆	0.6103	1.96	1.93	1.4					
$nC_{14}-nC_{6}$	0.6556	1.76	1.80	-2.3					
nC ₁₅ -nC ₆	0.6938	1.62	1.68	-3.7					
$nC_{16}-nC_{6}$	0.7446	1.54	1.58	-2.6					
$nC_{17}-nC_6$	0.7737	1.46	1.52	-4.1					
$nC_{18}-nC_{6}$	0.8265	1.39	1.43	-2.9					
set 1: nC _i -nC ₁₀									
nC_5-nC_{10}	0.3993	3.03	2.96	2.3					
nC_6-nC_{10}	0.4704	2.54	2.51	1.2					
$nC_{7}-nC_{10}$	0.5633	2.09	2.09	-0.0					
nC_{14} - nC_{10}	1.2929	0.913	0.915	-0.2					
$nC1_{5}-nC_{10}$	1.3972	0.819	0.845	-3.1					
$nC_{16}-nC_{10}$	1.5150	0.756	0.779	-3.0					
$nC_{17} - nC_{10}$	1.6337	0.702	0.722	-2.8					
$nC_{18}-nC_{10}$	1.7780	0.656	0.664	-1.2					
set 1: nC _i -nC ₁₂									
$nC_5 - nC_{12}$	0.4551	2.57	2.59	-0.9					
nC_6-nC_{12}	0.5581	2.09	2.11	-1.2					
$nC_7 - nC_{12}$	0.6823	1.70	1.73	-1.7					
nC_8-nC_{12}	0.8071	1.49	1.46	1.9					
$nC_{9}-nC_{12}$	0.9452	1.24	1.25	-0.8					
nC_{16} - nC_{12}	2.0335	0.589	0.580	1.5					
$nC_{17}-nC_{12}$	2.2323	0.547	0.529	3.2					
$nC_{18}-nC_{12}$	2.3945	0.503	0.493	2.0					

 ${}^{a}(\overline{D_{12}})_{cc}$ is the diffusion coefficient calculated from eq 9, and δ is the relative deviation between D_{12} and D_{cc} .

Table 2. Diffusion Coefficient (D_{12}) in the nC_{12} - nC_{6} , nC_{12} - nC_{7} , and nC_{12} - nC_{8} Systems for Different Mass Fractions of nC_{12} (w_{1}) at 298 K^{*a*}

mixture	w_1	$D_{12} \ 10^{-9} \ {\rm m}^2 \ {\rm s}^{-1}$	$(D_{12})_{\rm cc} \ 10^{-9} \ {\rm m}^2 \ {\rm s}^{-1}$	δ (%)
nC ₁₂ -nC ₆	0.18	2.48	2.55	-3.0
	0.46	2.24	2.17	3.1
	0.50	2.13	2.11	0.7
	0.66	1.93	1.88	2.2
	0.82	1.72	1.67	2.9
	0.95	1.51	1.49	1.0
nC ₁₂ -nC ₇	0.16	2.09	2.04	2.6
	0.42	1.84	1.80	2.2
	0.50	1.70	1.73	-1.7
	0.63	1.64	1.61	1.6
	0.80	1.48	1.46	1.2
	0.94	1.37	1.33	2.9
nC ₁₂ -nC ₈	0.10	1.70	1.69	0.6
	0.40	1.56	1.52	2.5
	0.50	1.49	1.46	2.0
	0.80	1.25	1.28	-2.4

 $^{a}(D_{12})_{cc}$ is the diffusion coefficient calculated from eq 19, and δ is the relative deviation between calculated and measured diffusion coefficient.

parameter. To determine the constant parameter, *a*, five 188 mixtures of known concentration are prepared by weighing 189 and then, the density of each mixture is measured. Thus, we 190



Figure 2. Diffusion coefficient as a function of the inverse of the dynamic viscosity for the systems $nC_6 \cdot nC_i$ (\Box), $nC_{10} \cdot nC_i$ (O), and $nC_{12} \cdot nC_i$ (Δ), at 50 wt % and 298 K.

 $_{191}$ determined the mass fraction with a deviation around wt % \pm $_{192}$ 0.01.

¹⁹³ The dynamic viscosity (μ) of the studied mixtures has been ¹⁹⁴ measured with an Anton Paar AMVn falling ball Micro-¹⁹⁵ viscosimeter with reproducibility better than 0.1%. All the ¹⁹⁶ measurements were done at 298 K.

III. RESULTS AND DISCUSSION

A. Studied Mixtures. All of the products used in this study were purchased from Merck with a purity better than 99%. The studied mixtures have been prepared by weight using a Gram VXI-310 digital scale with a precision of 0.001 g. and introducing first the less volatile component and then the corresponding amount of the second component; the mixture is finally shaken to ensure homogeneity. After the preparation, the density of the mixture was measured to confirm that the composition deduced from the calibration curve coincides with the prepared one. This was always the case.



Figure 3. Diffusion coefficient as a function of the mass fraction of the denser component (nC_{12}) for the mixtures, nC_{12} - nC_6 , nC_{12} - nC_7 , and nC_{12} - nC_8 at 298 K. \blacksquare , nC_{12} - nC_6 this work; \Box , nC_{12} - nC_6 ref 22; \times , nC_{12} - nC_6 ref 24; \bigcirc , nC_{12} - nC_7 this work; \bigcirc , nC_{12} - nC_7 ref 23; \blacktriangle , nC_{12} - nC_8 this work; \bigcirc , nC_{12} - nC_7 ref 23; \bigstar , nC_{12} - nC_8 this work; \bigcirc , nC_{12} - nC_8 ref 21. The continuous lines represent a linear fit to the data.

In this study, 25 mixtures at 50 wt % have been prepared $_{207}$ corresponding to the *n*-alkane series $_{208}$

$$nC_6 - nC_i i = 10, 11, 12, 13, 14, 15, 16, 17, 18$$

 $nC_{10} - nC_{i}i = 5, 6, 7, 14, 15, 16, 17, 18$

Table 3. Values of the Limiting Diffusion Coefficient $(D_1^0$ and $D_2^0)$ Taken from Refs 3 and 23^{*a*}

system	D_1^0	D_2^0	D_{1}^{0}/D_{2}^{0}	M_1/M_2	$\delta(\%)$
nC ₁₆ -nC ₆	2.21	0.85	2.60	2.62	0.7
nC ₁₂ -nC ₆	2.74	1.42	1.93	1.97	2.5
$nC_{12}-nC_7$	2.19	1.30	1.69	1.70	0.6
$nC_{12}-nC_8$	1.71	1.15	1.49	1.49	0.0
nC ₁₆ -nC ₁₂	0.67	0.49	1.36	1.33	-2.2
$nC_{7}NC_{8}$	2.80^{b}	2.43 ^b	1.15	1.14	-1.7

^{*a*} M_1 and M_2 are the molecular masses of the components, and δ is the relative deviation between the ratios D_1^0/D_2^0 and M_1/M_2 . ^{*b*}Interpolated from ref 3.

 $nC_{12} - nC_{i}i = 5, 6, 7, 8, 9, 16, 17, 18$

The measured values at 298 K for dynamic viscosity (μ) and 209 mass diffusion coefficients for these mixtures are summarized in 210 Table 1.

In addition, this study has been completed measuring the 212 molecular diffusion coefficient of the systems nC_{12} - nC_6 , nC_{12} - 213 nC_7 , and nC_{12} - nC_8 at 298 K at different concentrations. For 214 this end, the following mixtures were prepared: 215

$$nC_{12} - nC_6 w_1 = 0.18, 0.46, 0.50, 0.66, 0.82, 0.95.$$

$$nC_{12} - nC_7 w_1 = 0.16, 0.42, 0.50, 0.63, 0.80, 0.94.$$

$$nC_{12} - nC_8 w_1 = 0.10, 0.40, 0.50, 0.80.$$

where w_1 is the mass fraction of dodecane.

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In Table 2, the measured values of the diffusion coefficients ²¹⁷ of these systems at the concentrations considered are shown. ²¹⁸

These systems were chosen, as hydrocarbon mixtures are 219 quite regular in their properties. It was hoped that at least some 220 general and useful empirical relationship would be found. 221



Figure 4. Experimental diffusion coefficient versus calculated from eq 19 diffusion coefficient. ×, nC_{10} - nC_7 ref 23; O, nC_{12} - nC_6 ref 22; \Diamond , nC_{12} - nC_6 ref 24; ∇ , nC_{12} - nC_7 ref 23; Δ , nC_{12} - nC_8 ref 21; +, nC_{14} - nC_7 ref 23; ×, nC_{14} - nC_8 ref 23; *, nC_{16} - nC_7 ref 22.

B. Correlation between Diffusion and Viscosity. In what follows, we shall analyze the relation between the diffusion coefficient and the dynamic viscosity for mixtures at a mass practice equal to 50 wt % (equimass mixtures).

In Figure 2, the values of D_{12} as a function of the inverse of dynamic viscosity for the equimass mixtures in Table 1 are represented. As can be seen, the data fit well to a straight line, which passes through the origin and, thus, the following linear read relation can be written:

$$\overline{D_{12}} = k \frac{1}{\overline{\mu}} \tag{9}$$

²³¹ where $\overline{D_{12}}$ and $\overline{\mu}$ are the diffusion coefficient and the dynamic ²³² viscosity at $w_1 = 0.5$, respectively. The proportionality constant ²³³ k is $k = 1.18 \times 10^{-12}$ kg m/s².

In Table 1, the values of $\overline{D_{12}}$ calculated using eq 9 for each mixture are also shown and in the last column, the relative deviations with the measured values are given. As can be seen, these deviations are smaller than 3% in all the cases. Thus, we can conclude that the product $\overline{D_{12}}\mu$ for equimass mixtures is a universal constant for *n*-alkane mixtures.

D. Dependence of the Diffusion Coefficient with 240 241 Composition. According to Darken equation for thermody-242 namic ideal mixtures, the diffusion coefficient should be a linear 243 function of the molar fraction. However, as was suggested in an 244 earlier work by van Geet and Adamson,²¹ the diffusion coefficient 245 in n-alkane mixtures is linear with the mass fraction but not with 246 the mole fraction. To closely analyze the diffusion composition 247 dependence we have measured the diffusion coefficient as a 248 function of composition for the three systems: nC_{12} - nC_{6} , nC_{12} -249 nC_{72} and nC_{12} - nC_8 . The results obtained appear in Table 2. In 250 Figure 3, these data as a function of the mass fraction of the 251 heavier component, w₁, are plotted. As can be seen, the ordinary 252 diffusion coefficient is for each system a linear function of the 253 mass fraction and decreases with the concentration of the heavier 254 component. In this figure, the diffusion data in the literature for 255 the systems considered 21-24 are also shown. These data coincide with our measurements within the experimental error. 256

 $_{257}$ Thus, the dependence of D_{12} with composition can be $_{258}$ written as follows:

$$D_{12} = w_2 D_1^0 + w_1 D_2^0 \tag{10}$$

259 where w_1 and w_2 are the mass fraction of heavier and lighter 260 components, respectively, and D_1^0 and D_2^0 are the limiting 261 diffusion coefficients defined by

$$D_1^0 = \lim_{w_1 \to 0} D_{12} \tag{11}$$

$$D_2^0 = \lim_{w_2 \to 0} D_{12} \tag{12}$$

²⁶² In Table 3, the values of D_1^0 and D_2^0 for some selected mixtures ²⁶³ reported in the literature^{3,23} covering a large range of mass ratio for ²⁶⁴ liquid n-alkanes are given. As can be seen in this table, the ratio ²⁶⁵ D_1^0/D_2^0 is always close to the ratio of the molecular masses M_1/M_2 ²⁶⁶ of the two alkanes involved. Thus, we have

$$\frac{D_1^0}{D_2^0} = \frac{M_1}{M_2} \tag{13}$$

Introducing eq 13 in eq 10, one obtains

$$D_{12} = D_1^0 \left(w_2 + \frac{M_2}{M_1} w_1 \right) \tag{14}$$

For $w_1 = w_2 = 0.5$, the corresponding diffusion coefficient $\overline{D_{12}}$ will be 268

$$\overline{D_{12}} = \frac{D_1^0}{2} \left(\frac{M_1 + M_2}{M_1} \right)$$
(15)

and then, eq 14 in terms of $\overline{D_{12}}$ can be written as

$$D_{12} = 2 \overline{D_{12}} \left(\frac{M_1 w_2 + M_2 w_1}{M_1 + M_2} \right)$$
(16)

In particular, the infinite dilution values D_1^{0} and D_2^{0} will be 270

$$D_1^0 = 2 \overline{D_{12}} \frac{M_1}{M_1 + M_2} \tag{17}$$

$$D_2^0 = 2 \overline{D_{12}} \frac{M_2}{M_1 + M_2} \tag{18}$$

Finally, using eq 9, the diffusion coefficient can be written as 271

$$D_{12} = \frac{2k}{\overline{\mu}} \left(\frac{M_1 w_2 + M_2 w_1}{M_1 + M_2} \right)$$
(19)

where $k = 1.18 \times 10^{-12} \text{ kg m/s}^2$. 272

Equation 16 allows determining D_{12} from $\overline{D_{12}}$ measurements, 273 which, in turn, can be calculated using eq 9 from viscosity 274 measurements. 275

To confirm the validity of this correlation, we have 276 determined the values of D_{12} from eq 19 for the mixtures 277 given in Table 2. As shown in the last column of this table, the 278 relative deviations between these values and the experimental 279 ones are inferior to the experimental error. 280

As an additional test of eq 19, we have taken the ²⁸¹ experimental D_{12} values as a function of concentration reported ²⁸² in the literature²¹⁻²⁴ for different *n*-alkane systems. In Figure 4, ²⁸³ the values of D_{12} calculated using eq 19 are plotted against the ²⁸⁴ corresponding experimental ones. As seen here, all data lie on a ²⁸⁵ straight line through the origin with slope unity. ²⁸⁶

From what has been just mentioned, we can conclude that 287 the diffusion coefficient of *n*-alkane mixtures at any concentra- 288 tion can be calculated from the data of dynamic viscosity for 289 equimass mixtures. 290

IV. CONCLUSIONS

In this work, the diffusion coefficient of several n-alkane 291 mixtures at 50 wt % has been measured by using the SST 292 technique. From the results obtained, it is shown that the 293 product of the diffusion coefficient and the dynamic viscosity 294 for these mixtures is a universal constant independent of the 295 alkane involved. 296

In addition, the diffusion coefficient of the systems nC_{12} - nC_{6} , 297 nC_{12} - nC_{7} , and nC_{12} - nC_{8} in the whole concentration range has 298 also been measured. We have obtained for each system a linear 299 correlation between the diffusion coefficient and the mass 300 fraction. This correlation allows determining the diffusion 301 coefficient at any concentration from the molecular weight of 302 the components of a mixture and the dynamic viscosity of the 303 mixture at 50 wt %.

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315 **REFERENCES**

- 316 (1) Fick, A. Poggendorff's Ann. Phys. 1855, 94, 59.
- 317 (2) Cussler, E. Diffusion Mass Transfer in Fluid Systems; Cambridge 318 Univesity Press: New York, 1997.

(3) Alizadeh, A. A.; Wakeham, W. A. Int. J. Themophys. 1982, 3 (4),
 307.

- 321 (4) Dutrieux, J.; Platten, J. K.; Chavepeyer, G.; Bou-Ali, M. M. J. Phys. 322 Chem. B **2002**, *106*, 6104.
- 323 (5) Wiegand, S.; Köhler, W. *Thermal Nonequilib. Phenom. Fluid Mixt.*; 324 Springer: Berlin, 2002; pp 36–43.
- 325 (6) Taylor, R.; Krishna, R. *Multicomponent mass transfer*; John Wiley 326 & Sons Inc.: New York, 1993.
- (7) Cussler, E. *Multicomponent diffusion*; Elsevier Scientific PublishingCompany: Amsterdam, 1976.
- 329 (8) Rutten, P. W. M. *Diffusion in liquids*; Delft University Press: Delft, 330 1992.
- 331 (9) Tyrrell, J. V. Harris, K. R. *Diffusion in liquids*; Butterworth & Co., 332 Ltd.: London, 1984.
- 333 (10) Leahy-Dios, A.; Bou-Ali, M. M.; Platten, J. K.; Firoozabadi, A. 334 J. Chem. Phys. **2005**, 122, 234502.
- 335 (11) Ghorayeb, K.; Firoozabadi, A. AIChE J. 2000, 46, 883-891.
- 336 (12) Polyakov, P.; Müller-Plathe, F.; Wiegand, S. J. Phys. Chem. B 337 **2008**, 112, 14999.
- 338 (13) Blanco P.; Bou-Ali M. M.; Urteaga P.; Alonso de Mezquia D.; 339 Platten J. K. Sliding Symmetric Tubes: new technique for the 340 molecular diffusion coefficients determination of liquid mixtures. 18th 341 European Conference on Thermophysical Properties, Pau, France, 342 2008.
- 343 (14) Alonso de Mezquia D.; Blanco, P.; Bou-Ali M. M.; Zebib A.
- 344 New Technique for Measuring the Molecular Diffusion Coefficients of 345 Binary Liquid Mixtures. *European Thermodynamics Seminar EURO*-346 *THERM* 84, Namur, Belgium, **2009**.
- 347 (15) Blanco P., Bou-Ali M. M., Urteaga P.; Tubos Simétricos
- 348 Deslizantes, Patente P200700132/2, 2008.
- 349 (16) Platten, J. K.; Bou-Ali, M. M.; Costesèque, P.; Dutrieux, J.;
- 350 Köhler, W.; Leppla, C.; Wiegand, S.; Wittko, G. *Philos. Mag.* **2003**, *83*, 351 1965.
- 352 (17) Leahy-Dios, A.; Firoozabadi, A. J. Phys. Chem. B 2007, 111, 191.
- 353 (18) Zhang, K. J.; Briggs, M. E.; Gammon, R. W.; Sengers, J. V. 354 J. Chem. Phys. **1996**. 104, 6881.
- 355 (19) Kolodner, P.; Williams, H.; Moe, C. J. Chem. Phys. **1988**, 88, 356 6512.
- 357 (20) Köhler, W.; Müller, B. J. Chem. Phys. 1995, 103, 4367.
- 358 (21) Van Geet, L. A.; Adamson, W. A. J. Phys. Chem. 1964, 68 (2),
- 359 238.
 360 (22) Bidlack, D. L.; Anderson, D. K. J. Phys. Chem. 1964, 68, 3790.
- (22) Bidlack, D. L.; Anderson, D. K. J. Phys. Chem. 1964, 68, 3790.
 (23) Lo, H. Y. Chem. Eng. Data Ser. 1974, 19 (3), 236–241.
- (25) EO, II. I. Chem. Eng. Dutt Sci. 1974, 19 (3), 230–241.
 (24) Shieh, J. J. C.; Lyons, P. A. J. Phys. Chem. 1969, 73, 3258.