

Determination of the molecular diffusion coefficients in ternary mixtures by the sliding symmetric tubes technique

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A new analytical methodology has been developed to determine the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures by the Sliding Symmetric Tubes technique. The analytical solution is tested in binary mixtures obtaining good agreement with the results of the literature. Results are presented for the ternary mixture formed by tetralin, isobutylbenzene, and dodecane with an equal mass fraction for all the components (1–1–1) which is held at 25 °C. Diagonal and cross-diagonal coefficients are determined for the three possible orders of components, in order to compare the results with those available in the literature. A comparison with published results shows a good agreement for the eigenvalues of the diffusion matrix, and a reasonable agreement for the diagonal molecular diffusion coefficients. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4864189>]

I. INTRODUCTION

The phenomenon of molecular diffusion in multicomponent mixtures has attracted a great interest within the scientific community, and it has been analyzed in multiple processes of different sectors, such as human biology,¹ materials engineering,² or food industry.³

In 1855, Fick established the first quantitative relation for molecular diffusion, known as Fick's law,⁴ and since then different experimental procedures have been developed in order to determine the molecular diffusion coefficient. In the case of binary mixtures, this phenomenon has been studied in depth and currently there are many well-established and proven experimental techniques which allow the determination of this coefficient. Among them are Thermal Diffusion Forced Rayleigh Scattering (TDFRS) (Ref. 5), Open Ended Capillary (OEC) (Ref. 6), Optical Beam Deflection,⁷ Optical Digital Interferometry,⁷ techniques that use the Taylor dispersion principle,⁸ and the Sliding Symmetric Tubes (SST) technique.⁹

In the case of ternary mixtures, the existence of diagonal and cross-diagonal molecular diffusion coefficients makes their determination considerably more difficult. In the last few years, several works have been published in which the determination of these molecular diffusion coefficients has been attempted; however, the availability of results in the literature is limited, so currently, the reliability of these methods has still to be tested. For example, Königer *et al.*¹⁰ tried to solve the problem applying a second wavelength for the determination by the Two Colour Optical Beam Deflection technique; Mialdun *et al.*¹¹ devised a new instrument based on interferometry to determine the molecular diffusion coefficients. Leahy-Dios *et al.*¹² used the OEC technique combining the

density and refractive index measurements for the determination of the molecular diffusion coefficients and Santos *et al.*¹³ and Capuano *et al.*¹ used the Taylor dispersion principle and the Gouy interferometer, respectively. In addition, simulations based on molecular dynamics¹⁴ and prediction models³ have been undertaken in order to determine the molecular diffusion coefficients in ternary mixtures. In Larrañaga *et al.*,¹⁵ an analytical solution applied to SST technique was developed to determine the diffusion coefficients in ternary mixtures. Recently, Mialdun *et al.*¹⁶ have published a new paper determining the molecular diffusion coefficients in ternary mixtures by two independent experimental techniques: Taylor dispersion technique and digital interferometry applied to a Counter Flow Cell.

As commented in Mialdun and Shevtsova,¹⁷ the correct determination of the molecular diffusion coefficients is very important for the determination of the thermodiffusion coefficients because, except in the case of the thermogravitational column, in the other techniques it is necessary to consider these two diffusion coefficients combined with Soret coefficient, so that the thermodiffusion coefficient for each component may be determined.

Therefore, the principal objective of the present work is the determination of the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures by the SST technique. To this end, the mixture formed by 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB), and n-dodecane (nC12), with equal mass fraction and at 25 °C has been used. This mixture was selected by the group which takes part in the project DCMIX (Ref. 18) and which is formed by 14 teams at international level in order to perform analytical, numerical, and experimental studies both in terrestrial conditions and in microgravity, by the installation Selectable Optical Diagnostic Instrument (SODI) in the International Space Station and by applying a purely optical analysis system based on two wavelengths.

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87 This article is organized as follows. In Sec. II, the
 88 methodology, both experimental and analytical, for the deter-
 89 mination of the molecular diffusion coefficients by the SST
 90 technique is described. In Sec. III, experimental results ob-
 91 tained for both binary and ternary mixtures and the discus-
 92 sion about them are presented. Finally, conclusions are given
 93 in Sec. IV.

94 II. METHODOLOGY

95 A. Experimental procedure

96 The SST technique has been successfully applied in the
 97 case of binary mixtures¹⁹⁻²¹ and it consists of several sets
 98 of tubes (Figure 1) which have two positions. In the faced
 99 tubes position, the contents of both tubes are in contact and
 100 the transport of matter between the tubes arises by molecu-
 101 lar diffusion. By contrast, in the separated tubes position the
 102 diffusive process is stopped. All the tubes are filled with the
 103 same mixture, but with a slight difference of concentration
 104 between the upper and bottom tubes. In an experiment, all the
 105 sets of tubes are filled in the separated tubes position and they
 106 are introduced into a water bath (see Figure 2) with a temper-
 107 ature control of 0.1 °C, which will maintain them at the same
 108 temperature throughout the whole experiment. At the begin-
 109 ning of the experiment all the sets are changed to the faced
 110 tubes position so that diffusion may be initiated. From that
 111 moment, at various predetermined intervals of time, each tube
 112 is changed to the separated tubes position, to preserve their
 113 contents for later analysis. At the end of the experiment, the
 114 variation of the concentration with time is constructed from
 115 the concentrations in each of the tubes (see Figure 3).

116 In order to determine the concentration of each point in a
 117 ternary mixture, its density and refractive index are measured
 118 by an Anton Paar DMA 5000 vibrating quartz U-tube den-
 119 simeter with an accuracy of 5×10^{-6} g/cm³ and by an Anton
 120 Paar RXA 156 refractometer with an accuracy of 2×10^{-5}

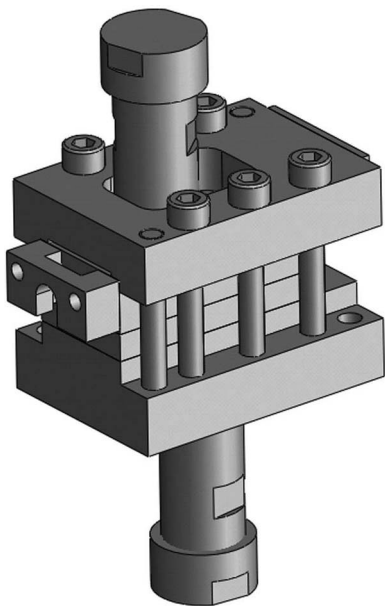


FIG. 1. A set of sliding symmetric tubes.

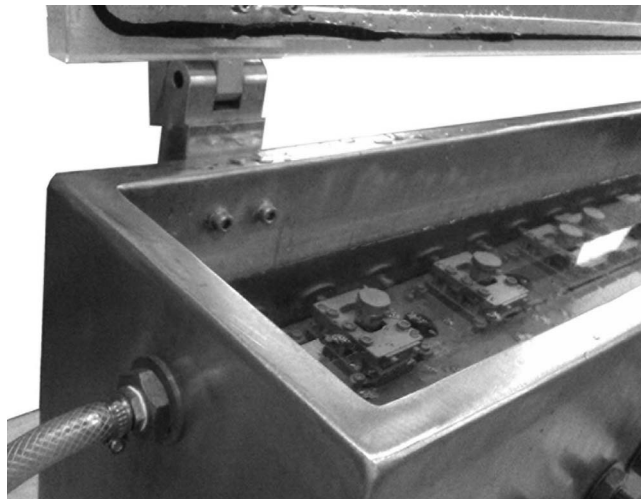


FIG. 2. Installation of the sliding symmetric tubes technique.

121 RIU, respectively. Mialdun and Shevtsova¹⁷ and Sawicka and
 122 Soroka²² show that these two properties allow the most accu-
 123 rate determination of the concentration of each component. In
 124 order to determine the concentration from the density and the
 125 refractive index it is necessary to do a prior calibration where
 126 measurements are made of the density and the refractive in-
 127 dex of 25 mixtures with concentrations that are close to that
 128 of the study. Once the calibration coefficients are determined,
 129 the concentration of each component, w_i , in each point is cal-
 130 culated by the following equations:

$$w_1 = \frac{c'(\rho - a) - c(n_D - a')}{bc' - b'c}, \quad (1)$$

$$w_2 = \frac{b(n_D - a') - b'(\rho - a)}{bc' - b'c}, \quad (2)$$

$$w_3 = 1 - w_1 - w_2, \quad (3)$$

131 where ρ and n_D are the density and the refractive index,
 132 respectively, and a , a' , b , b' , c , and c' are the calibration
 133
 134

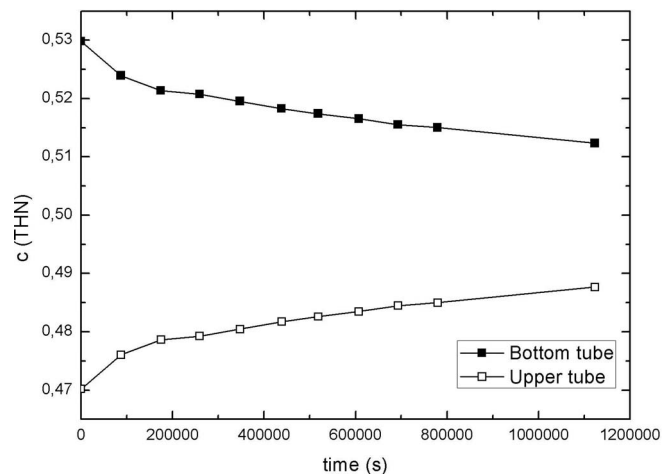


FIG. 3. Variation of the concentration with time in the upper and the bottom tubes determined by the SST technique, for the mixture THN-IBB with 50% mass fraction and at 25 °C.

135 parameters calculated for the mixture (see Larrañaga *et al.*¹⁵
136 for details).

137 B. Analytical solution

138 First, an analytical solution for binary mixtures was de-
139 veloped, which allowed the determination of the molecular
140 diffusion coefficient from the experimental measurements of
141 the variation of the concentration with time.¹⁹ The working
142 equations are the following:

$$w^{bot} |_{m(t)} = \frac{w_i^{bot} + w_i^{up}}{2}$$

$$= \frac{4}{\pi^2} \cdot (w_i^{bot} - w_i^{up}) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot D \cdot t}}{(2n+1)^2}, \quad (4)$$

$$w^{up} |_{m(t)} = \frac{w_i^{bot} + w_i^{up}}{2}$$

$$= \frac{4}{\pi^2} \cdot (w_i^{up} - w_i^{bot}) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot D \cdot t}}{(2n+1)^2}, \quad (5)$$

143 where $w^{up} |_{m(t)}$ and $w^{bot} |_{m(t)}$ are the mean concentration in
144 the upper and lower tubes respectively, as functions of time;
145 w_i^{up} and w_i^{bot} are the respective initial concentrations, D is the
146 molecular diffusion coefficient, which is constant in the case
147 of small concentration variations, and L is the length of the
148 tube.

149 As may be noted, the formulae given in Eqs. (4) and
150 (5) are linearly dependent and therefore it follows, not sur-
151 prisingly, that the molecular diffusion coefficient must be the
152 same in both tubes for binary mixtures.

153 In Larrañaga *et al.*,¹⁵ an initial analytical solution for
154 ternary mixtures was obtained by following the same Fourier
155 series procedure as for the case of binary mixtures. The evo-
156 lution of the mean concentration of component j was found to
157 take the following form:

$$\phi_j^{bot} |_{m(t)} = \frac{\phi_{ji}^{bot} + \phi_{ji}^{up}}{2}$$

$$= \frac{4}{\pi^2} \cdot (\phi_{ji}^{bot} - \phi_{ji}^{up}) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_j \cdot t}}{(2n+1)^2}, \quad (6)$$

$$\phi_j^{up} |_{m(t)} = \frac{\phi_{ji}^{bot} + \phi_{ji}^{up}}{2}$$

$$= \frac{4}{\pi^2} \cdot (\phi_{ji}^{up} - \phi_{ji}^{bot}) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_j \cdot t}}{(2n+1)^2}, \quad (7)$$

158 for $j = 1, 2$ and where $\phi_j^{up/bot} |_{m(t)}$ is the new variable for
159 the mean concentration in the upper and the lower tubes, re-
160 spectively, $\phi_{ji}^{up/bot}$ is the new variable for the initial concen-
161 tration in the upper and the lower tubes, respectively, and the
162 λ_j -values are the eigenvalues of the diffusion matrix.

163 As may be observed, these equations have now become
164 considerably more complicated and in this case there are two
165 linearly independent equations (for each components 1 and 2)
166 with four unknowns (the two diagonal diffusion coefficients
167 and another two cross-diagonal diffusion coefficients). That

170 is why a nonlinear fitting had to be applied in order to de-
171 termine the diffusion coefficients. Before applying the fitting,
172 the changes of variable were undone, so that the equations be-
173 came more complicated but we could fit directly the four dif-
174 fusion coefficients. However, the complexity of the equations
175 made it impossible to achieve reliable results with different
176 fitting methods, as is detailed in Larrañaga *et al.*¹⁵

177 That difficulty has motivated the development of a new
178 analytical solution which allows the determination of the
179 diffusion coefficients for both binary and ternary mixtures.
180 The new analytical solution is based on the well-known
181 self-similar solution of Fourier's equation for an impulsively
182 heated solid which is found in Carslaw and Jaeger,²³ and it is
183 described hereafter; the method is illustrated first for binary
184 mixtures and then it is extended to ternary mixtures.

185 C. New analytical solution for binary mixtures

186 It is intended to solve Fick's second law,

$$\frac{\partial w}{\partial t} = D \cdot \frac{\partial^2 w}{\partial y^2}, \quad (8)$$

187 for relatively short times, by which we mean that the devel-
188 oping interface between the upper and lower tubes has not
189 yet reached the far ends of those tubes. In this regime, the
190 evolving front satisfies a self-similar solution for which the
191 following changes of variable are required:

$$\eta = \frac{y}{2\sqrt{Dt}}, \quad (9)$$

$$\tau = \sqrt{t}, \quad (10)$$

192 where y is the vertical variable. While within the self-similar
193 regime the time-derivative may be neglected and therefore the
194 equation for the concentration transforms to

$$w'' + 2\eta w' = 0, \quad (11)$$

195 where w' and w'' are the first and the second derivatives of the
196 concentration with respect to η .

197 The boundary conditions in this case, taking into account
198 the variable transformation, are the following:

$$w \rightarrow w_i^{bot} \text{ as } \eta \rightarrow -\infty, \quad (12)$$

$$w \rightarrow w_i^{up} \text{ as } \eta \rightarrow +\infty,$$

199 where w_i^{up} and w_i^{bot} are the initial concentration in the up-
200 per and lower tubes, respectively. Upon solving Eq. (11), the
201 following expression for the concentration is obtained:

$$w = w_i^{up} + \frac{w_i^{bot} - w_i^{up}}{2} \operatorname{erfc}(\eta), \quad (13)$$

202 where $\operatorname{erfc}(\eta)$ is the well-known complementary error func-
203 tion of η .²³

204 The mean concentration in each tube is obtained by in-
205 tegrating the solution given in Eq. (13) over the length of the
206 tube, and then dividing it by the length of the tube, L ,

$$\frac{1}{L} \int_0^L w \, dy = w_i^{up} + \frac{(w_i^{bot} - w_i^{up})}{L} \sqrt{\frac{Dt}{\pi}}. \quad (14)$$

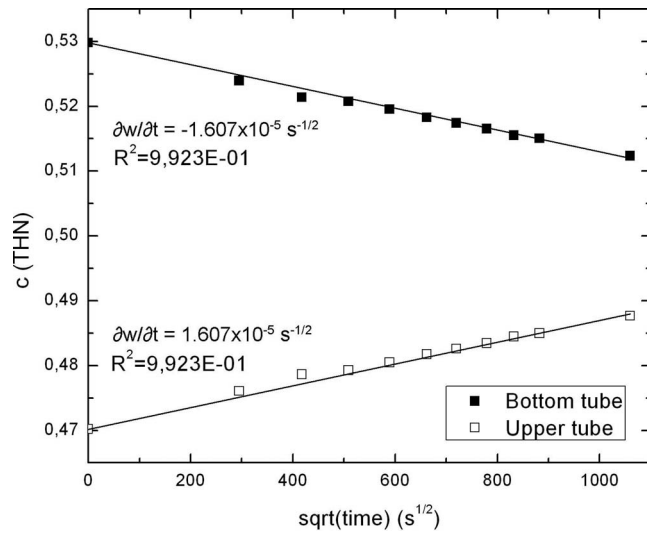


FIG. 4. Variation of the concentration with the square root of time for the mixture THN-IBB at 50% of mass fraction at 25 °C.

It is important to note that Eq. (14) remains valid until the diffusion front (i.e., the region of mixing between the two reservoirs) begins to reach the ends of the tubes. Equation (14) shows that the mean concentration varies linearly with $t^{1/2}$ and therefore Figure 4 has been created to show this linear variation of the upper and lower mean concentrations with the square root of time for the mixture THN-IBB with mass fraction of 50% and at 25 °C. As can be seen, the variations are almost linear and therefore the molecular diffusion coefficient as given by the upper tube data may be determined directly by the following expression:

$$S^{up} = \frac{(w_i^{bot} - w_i^{up})}{L} \sqrt{\frac{D}{\pi}}, \quad (15)$$

where S^{up} is the slope of the linear regression formed by the concentration points in the upper tube. If the slope formed by the concentration points in the lower tube is taken, then the diffusion coefficient which is obtained is the same. The presence of linearity in Figure 4 also shows that the diffusion front has not reached the ends of the tubes, and therefore the self-similar solution given in (13) is valid.

D. New analytical solution for ternary mixtures

In the case of ternary mixtures, the procedure is similar to the case of binary mixtures, but it is necessary to use a second change of variable in order to account for the presence of two different eigensolutions of the diffusion matrix, as will be seen. For ternary mixtures, Fick's second law may be written as follows:

$$\frac{\partial w_1}{\partial t} = D_{11} \cdot \frac{\partial^2 w_1}{\partial y^2} + D_{12} \cdot \frac{\partial^2 w_2}{\partial y^2}, \quad (16)$$

$$\frac{\partial w_2}{\partial t} = D_{21} \cdot \frac{\partial^2 w_1}{\partial y^2} + D_{22} \cdot \frac{\partial^2 w_2}{\partial y^2}, \quad (17)$$

where D_{11} and D_{22} are the diagonal diffusion coefficients and D_{12} and D_{21} are the cross-diagonal diffusion coefficients. The

variable changes applied in this case are the following:

$$\eta = \frac{y}{2\sqrt{t}}, \quad (18)$$

$$\tau = \sqrt{t}, \quad (19)$$

$$z = \alpha\eta, \quad (20)$$

where α is an eigenvalue which is to be found. Once more we assume that the diffusion front has not reached the extreme ends of the tubes, and therefore the following self-similar equations are obtained for the concentrations of the components 1 and 2:

$$D_{11}\alpha^2 w_1'' + 2z w_1' + D_{12}\alpha^2 w_2'' = 0, \quad (21)$$

$$D_{21}\alpha^2 w_1'' + D_{22}\alpha^2 w_2'' + 2z w_2' = 0, \quad (22)$$

where primes now denote derivatives with respect to the variable z .

The boundary conditions in this case are similar to the ones in the case of binary mixtures:

$$\begin{aligned} w_1 &\rightarrow w_{i1}^{bot} \text{ and } w_2 \rightarrow w_{i2}^{bot} \text{ as } \eta \rightarrow -\infty, \\ w_1 &\rightarrow w_{i1}^{up} \text{ and } w_2 \rightarrow w_{i2}^{up} \text{ as } \eta \rightarrow +\infty, \end{aligned} \quad (23)$$

where w_{i1}^{up} , w_{i1}^{bot} , w_{i2}^{up} , and w_{i2}^{bot} are the initial conditions of the components 1 and 2 in the upper and lower tubes, respectively.

Upon solving Eqs. (21) and (22), the following expressions are obtained for the concentrations of the two components:

$$w_1 = A \operatorname{erfc}(z_1) + B \operatorname{erfc}(z_2) + w_{i1}^{up}, \quad (24)$$

$$\begin{aligned} w_2 = A &\left(\frac{1 - D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) \operatorname{erfc}(z_1) \\ &+ B \left(\frac{1 - D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \operatorname{erfc}(z_2) + w_{i2}^{up}, \end{aligned} \quad (25)$$

where the constants A and B are given by the following functions of the diffusion coefficients and the initial concentrations of the components 1 and 2 in the upper and the lower tubes:

$$A = \frac{D_{12}\alpha_1^2\alpha_2^2(w_{i2}^{bot} - w_{i2}^{up}) - \alpha_1^2(w_{i1}^{bot} - w_{i1}^{up})(1 - D_{11}\alpha_2^2)}{2(\alpha_2^2 - \alpha_1^2)}, \quad (26)$$

$$B = \frac{D_{12}\alpha_1^2\alpha_2^2(w_{i2}^{bot} - w_{i2}^{up}) - \alpha_2^2(w_{i1}^{bot} - w_{i1}^{up})(1 - D_{11}\alpha_1^2)}{2(\alpha_1^2 - \alpha_2^2)}, \quad (27)$$

the values α_1 and α_2 , which are proportional to the eigenvalues of the diffusivity matrix, are given by

$$\alpha_1 = \sqrt{\frac{-(D_{11} + D_{22}) - \sqrt{(D_{11} + D_{22})^2 + 4(D_{12}D_{21} - D_{11}D_{22})}}{2(D_{12}D_{21} - D_{11}D_{22})}}, \quad (28)$$

$$\alpha_2 = \sqrt{\frac{-(D_{11} + D_{22}) + \sqrt{(D_{11} + D_{22})^2 + 4(D_{12}D_{21} - D_{11}D_{22})}}{2(D_{12}D_{21} - D_{11}D_{22})}}, \quad (29)$$

and

$$z_1 = \alpha_1 \eta, \quad (30)$$

$$z_2 = \alpha_2 \eta. \quad (31)$$

As in the case of binary mixtures, the expressions given in Eqs. (24) and (25) are integrated and then divided by the length of each tube to give the mean concentration for each component in each of the tubes:

$$\frac{1}{L} \int_0^L w_1 dy = w_{i1}^{up} + \frac{2}{L} \sqrt{\frac{t}{\pi}} \left(\frac{A}{\alpha_1} + \frac{B}{\alpha_2} \right), \quad (32)$$

$$\begin{aligned} \frac{1}{L} \int_0^L w_2 dy \\ = w_{i2}^{up} + \frac{2}{L} \sqrt{\frac{t}{\pi}} \left(\frac{A}{\alpha_1} \left(\frac{1 - D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) + \frac{B}{\alpha_2} \left(\frac{1 - D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \right). \end{aligned} \quad (33)$$

Equations (32) and (33) show that, in the case of ternary mixtures, the concentration of each component also varies linearly with the square root of time. Equations (32) and (33) may be therefore manipulated as before to give the slope of the line corresponding to each component:

$$S_1 = \frac{2}{L\sqrt{\pi}} \left(\frac{A}{\alpha_1} + \frac{B}{\alpha_2} \right), \quad (34)$$

$$S_2 = \frac{2}{L\sqrt{\pi}} \left(\frac{A}{\alpha_1} \left(\frac{1 - D_{11}\alpha_1^2}{D_{12}\alpha_1^2} \right) + \frac{B}{\alpha_2} \left(\frac{1 - D_{11}\alpha_2^2}{D_{12}\alpha_2^2} \right) \right), \quad (35)$$

where S_1 and S_2 are the slopes formed by the linear regression of the concentration of components 1 and 2, respectively, with respect to the square root of time.

In order to determine the molecular diffusion coefficients in ternary mixtures, it is necessary to have experimental data from two independent experiments of the same mixture where the initial concentrations are different. In this way, a system of four equations (i.e., Eqs. (34) and (35) for two different experiments) and four unknowns (the four diffusion coefficients) is obtained. It is impossible to solve for the four coefficients analytically because the four equations are highly nonlinear, but they may be found very rapidly using a straightforward four-dimensional Newton-Raphson method.

III. RESULTS AND DISCUSSION

In this section, first the molecular diffusion coefficients in binary mixtures determined by the classical and new analytical solutions are shown and compared, and then, the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures are determined from the new analytical solution.

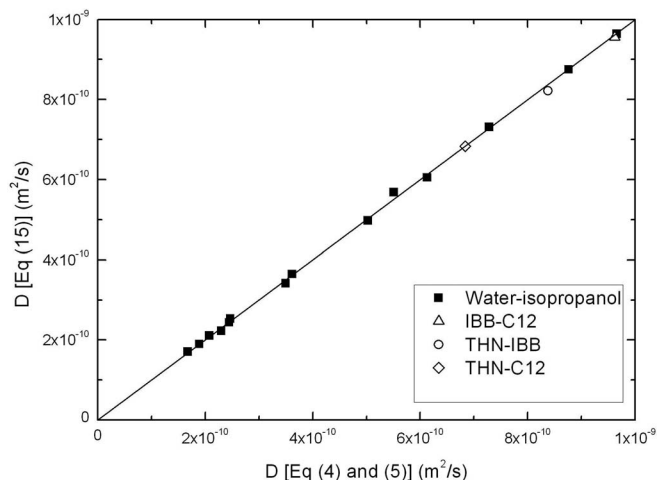


FIG. 5. Comparison of the results obtained by Eqs. (4) and (5), and Eq. (15) for the binary mixtures formed by THN, IBB, and n C12 with 50% of mass fraction and the mixture formed by water-isopropanol for many different mass concentrations of water; all cases are at 25 °C.

A. Binary mixtures

In previous works,^{19–21} the validity of the SST technique and the classical analytical solution (given by Eqs. (4) and (5)) for the determination of the molecular diffusion coefficients in binary mixtures have been shown to be accurate. Figure 5 compares the results obtained by the present new formulation (given by Eq. (15)) with the ones obtained by the classical solution (given by Eqs. (4) and (5)). The data used are for the binary mixtures formed by THN, IBB, and n C12 with 50% of mass fraction and at 25 °C, and for the mixture water-isopropanol for many different mass concentrations of water and at 25 °C.

The very good agreement between the results obtained by the two methods demonstrates the validity of the new analytical solution developed in this work, for the case of binary mixtures.

B. Ternary mixtures

In Larrañaga *et al.*,¹⁵ the determination of the diagonal and cross-diagonal molecular diffusion coefficients using the classical analytical solution (Eqs. (6) and (7)) was attempted. However, as has been pointed out, the establishment of a fitting method which allows reproducible results to be obtained and which does not depend on the fitting conditions was found to be impossible. By contrast, the new analytical solution developed in this work only requires a simple straight-line fit to obtain slopes and then the diffusion coefficients in ternary mixtures may be calculated directly by the Newton-Raphson method.

In this work, the results obtained for the ternary mixture THN-IBB- n C12 with equal mass fractions and at 25 °C are shown, and they are compared to the results published in the literature.

The experimental determination of the diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures requires experimental data from two independent

TABLE I. Initial concentrations and slopes, S ($s^{-1/2}$), for each component in the upper and the bottom tubes, in the two experiments carried out in this work, at 25 °C.

	Expt. 1	Expt. 2
w (THN) up	0.3033	0.3033
w (THN) bot	0.3633	0.3633
w (IBB) up	0.3433	0.3333
w (IBB) bot	0.3233	0.3333
w (C12) up	0.3533	0.3633
w (C12) bot	0.3133	0.3033
S (THN) up ($s^{-1/2}$)	1.58×10^{-5}	1.49×10^{-5}
S (THN) bot ($s^{-1/2}$)	-1.58×10^{-5}	-1.49×10^{-5}
S (C12) up ($s^{-1/2}$)	-0.96×10^{-6}	-1.43×10^{-5}
S (C12) bot ($s^{-1/2}$)	0.96×10^{-6}	1.43×10^{-5}

TABLE II. Molecular diffusion coefficients determined in this work for the mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C for the three possible orders of components.

Order of components $w_1-w_2-w_3$	$D_{11} \times 10^{-10}$ (m^2/s)	$D_{12} \times 10^{-10}$ (m^2/s)	$D_{21} \times 10^{-10}$ (m^2/s)	$D_{22} \times 10^{-10}$ (m^2/s)
THN-IBB- <i>n</i> C12	6.16	-4.61	0.37	11.40
THN- <i>n</i> C12-IBB	11.30	5.08	0.14	6.65
<i>n</i> C12-IBB-THN	6.54	-0.51	-0.37	11.06

into the corresponding forms for either of the other two possible choices of the components as shown in Königer *et al.*¹⁰

Because of the analysis method used in the present laboratory, the best accuracy was obtained when the components with highest and the lowest densities are chosen, and it is these that were generally chosen to be w_1 and w_2 . However, in order to compare the present results with those available in the literature, the molecular diffusion coefficients for all three possible orders of components have been determined experimentally. Table II shows the diagonal and cross-diagonal molecular diffusion coefficients for the three possible orders of components in the mixture.

In the three cases, the molecular diffusion coefficients satisfy the restrictions detailed in Mutoru *et al.*²⁴

The literature about molecular diffusion in ternary mixtures of hydrocarbons is very limited. For our same mixture and composition, there are only three works published. Königer *et al.*¹⁰ determined the molecular diffusion coefficients using the two colour optical beam deflection technique (OBD), considering the component order *n*C12-IBB-THN. Mialdun *et al.*¹¹ measured the molecular diffusion coefficients by a counter flow cell fitted with an optical interferometry device (CFC), and the component order THN-IBB-*n*C12 was preferred. Afterwards, this same team published a new work¹⁶ where two independent techniques were used: the counter flow cell fitted with an optical interferometry device (CFC) and Taylor dispersion technique (TDT). This last work¹⁶ emerges as more confident for the team of Mialdun *et al.*; however, as the published results for molecular diffusion coefficients in ternary mixtures are limited, we have compared the results of the three works available in the literature.

Table III shows the eigenvalues of the diffusion matrix determined here by the SST technique (rows 2, 3, and 4) and the ones determined by OBD (Ref. 10) (row 5), CFC (Ref. 11)

TABLE III. Comparison between the eigenvalues of the diffusion matrix obtained in this work and the results of the literature.

Data source	Order of components $w_1-w_2-w_3$	$\hat{D}_1 \times 10^{-10}$ (m^2/s)	$\hat{D}_2 \times 10^{-10}$ (m^2/s)
Present study: SST	THN-IBB- <i>n</i> C12	6.51	11.10
	THN- <i>n</i> C12-IBB	6.49	11.50
	<i>n</i> C12-IBB-THN	6.50	11.11
OBD ¹⁰	<i>n</i> C12-IBB-THN	6.81	10.99
CFC ¹¹	THN-IBB- <i>n</i> C12	7.26	11.23
TDT ¹⁶	THN-IBB- <i>n</i> C12	6.82	9.9
CFC ¹⁶	THN-IBB- <i>n</i> C12	7.09	11.17

experiments where the initial concentrations are different. Table I shows the initial concentrations of each component in the two experiments used in this case.

As for the case of binary mixtures, the variation of the concentration with the square root of time is linear. Figure 6 shows some experimental results for the mixture THN-IBB-*n*C12 with equal mass fraction and 25 °C, corresponding to the experiment 1 of Table I.

Prior to showing further results, it is necessary to discuss the implications of the choice of the order of components in a ternary mixture. The four molecular diffusion coefficients which are found depend on which two components of the three are assigned to the variables w_1 and w_2 in the flux Eqs. (36) and (37). This is why special care needs to be taken when results from different scientific groups are compared:

$$J_1 = -\rho (D_{11} \nabla w_1 + D_{12} \nabla w_2), \quad (36)$$

$$J_2 = -\rho (D_{21} \nabla w_1 + D_{22} \nabla w_2). \quad (37)$$

However, it is quite straightforward to manipulate the pair of coupled Fick's equations for these two components

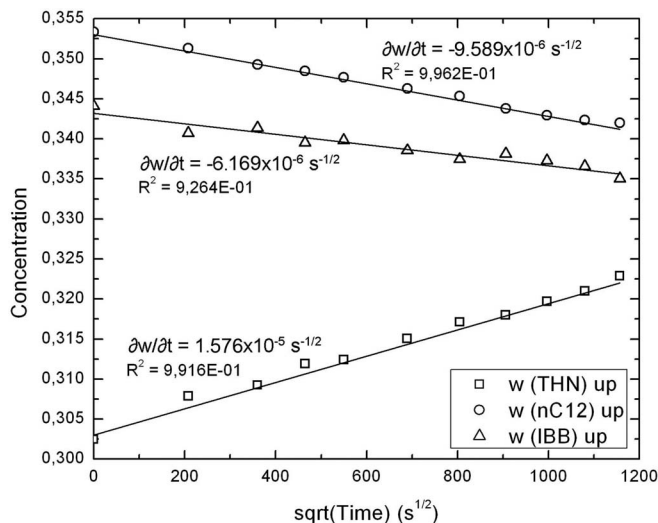


FIG. 6. Variation of the concentration with the square root of time for the components THN, IBB, and *n*C12 at 25 °C, obtained from the upper tube of the SST technique.

TABLE IV. Comparison of the diffusion coefficients for the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C, where THN and IBB form components w_1 and w_2 , respectively.

Data source	Order of components w_1 - w_2 - w_3	$D_{11} \times 10^{-10}$ (m ² /s)	$D_{12} \times 10^{-10}$ (m ² /s)	$D_{21} \times 10^{-10}$ (m ² /s)	$D_{22} \times 10^{-10}$ (m ² /s)
Present study: SST		6.16	-4.61	0.37	11.40
Present study: SST ^a		6.22	-5.08	0.28	11.73
OBD ^{10,a}	THN-IBB- <i>n</i> C12	5.62	-5.91	1.08	12.18
CFC ¹¹		6.92	1.06	-1.37	11.57
TDT ¹⁶		10.31	0.33	-4.36	6.41
CFC ¹⁶		11.61	0.32	-6.18	6.65

^aData have been transformed for the same order of components (Eqs. (A8)–(A11) in Königer *et al.*¹⁰).

TABLE V. Comparison of the diffusion coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C, where *n*C12 and IBB form components w_1 and w_2 , respectively.

Data source	Order of components w_1 - w_2 - w_3	$D_{11} \times 10^{-10}$ (m ² /s)	$D_{12} \times 10^{-10}$ (m ² /s)	$D_{21} \times 10^{-10}$ (m ² /s)	$D_{22} \times 10^{-10}$ (m ² /s)
Present study: SST		6.54	-0.51	-0.37	11.06
Present study: SST ^a		6.51	-0.14	-0.28	11.14
OBD ¹⁰	<i>n</i> C12-IBB-THN	6.70	0.43	-1.08	11.10
CFC ^{11,a}		5.55	-7.08	1.37	12.94
TDT ^{16,a}		5.95	-0.79	4.36	10.77
CFC ^{16,a}		5.43	-1.54	6.18	12.83

^aData have been transformed for the same order of components (Eqs. (A8)–(A11) in Königer *et al.*¹⁰).

TABLE VI. Comparison of the diffusion coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C, where THN and *n*C12 form components w_1 and w_2 , respectively.

Data source	Order of components w_1 - w_2 - w_3	$D_{11} \times 10^{-10}$ (m ² /s)	$D_{12} \times 10^{-10}$ (m ² /s)	$D_{21} \times 10^{-10}$ (m ² /s)	$D_{22} \times 10^{-10}$ (m ² /s)
Present study: SST		11.30	5.08	0.14	6.65
OBD ^{10,a}	THN- <i>n</i> C12-IBB	11.53	5.91	-0.43	6.27
CFC ^{11,a}		5.86	-1.06	7.08	12.63
TDT ^{16,a}		9.98	-0.33	0.79	6.74
CFC ^{16,a}		11.28	-0.32	1.55	6.97

^aData have been transformed for the same order of components (Eqs. (A8)–(A11) in Königer *et al.*¹⁰).

TABLE VII. Comparison of the Soret coefficients in the ternary mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C.

Data source	Order of components w_1 - w_2 - w_3	$S_T^{THN} \times 10^{-3}$ K ⁻¹	$S_T^{IBB} \times 10^{-3}$ K ⁻¹	$S_T^{nC12} \times 10^{-3}$ K ⁻¹
Present study: TGC + SST	THN-IBB- <i>n</i> C12	1.83	0.05	-1.88
	THN- <i>n</i> C12-IBB	1.82	0.07	-1.89
	<i>n</i> C12-IBB-THN	1.83	0.05	-1.88
OBD ¹⁰	<i>n</i> C12-IBB-THN	2.11	-0.96	-1.15

(row 6), TDT (Ref. 16), and CFC (Ref. 16) (rows 7 and 8). The second column indicates the order in which the components have been taken in each case. The eigenvalues of the diffusion matrix do not depend on the order of the components chosen, so they may be compared directly.

As can be observed, the agreement between the determined eigenvalues is reasonable, obtaining variations between 1% and 12%.

In order to make a comparison between the molecular diffusion coefficients obtained in this work and the ones published in the literature, in the three possible cases of order of components, the transformation of the diffusion matrix detailed in Eqs. (A8)–(A11) of Königer *et al.*¹⁰ has been applied to the results of this work and to the results of the literature, for the cases needed. Table IV shows the results found when the order of components is THN-IBB-*n*C12. Table V shows the results obtained when the order of components considered is *n*C12-IBB-THN. Finally, Table VI shows the results obtained in the case of considering the order of components THN-*n*C12-IBB.

As may be seen in Tables IV–VI, the agreement between the diagonal diffusion coefficients determined in this work and the ones published in the literature is reasonable in most of the cases, especially with the results shown in Königer *et al.*¹⁰ In the case of the cross-diagonal diffusion coefficients, the differences are bigger, appearing in some cases even a disagreement in the sign. The disagreements between the results of the different teams show the difficulty of the determination of the molecular diffusion coefficient in ternary mixtures. It is necessary to continue working in order to optimize the experimental techniques and the corresponding analysis methods. For that purpose, we plan to continue analyzing this mixture but in the whole range of concentrations.

In addition to the comparison of the molecular diffusion coefficients, it is also possible to compare the Soret coefficients of the mixture studied in this work. The Soret coefficient can be determined from the measurements of the thermodiffusion and the molecular diffusion coefficients, by the expression shown in Mialdun and Shevtsova¹⁷ In Blanco *et al.*,²⁵ this scientific team published the thermodiffusion coefficients for the mixture studied in this work determined by the thermogravitational technique (TGC). The molecular diffusion coefficients determined in this work by the SST technique allow determining Soret coefficients for the mixture THN-IBB-*n*C12 with equal mass fraction, at 25 °C. Table VII shows the results obtained in this work for the three different cases of order of components (rows 2–4) and the results determined experimentally by the OBD technique¹⁰ (row 5).

As may be observed, independently of the order of components chosen, the Soret coefficient corresponding to each coefficient is the same (rows 2–5 of Table VII). The agreement between the results obtained in this work and the ones shown in Königer *et al.*¹⁰ is optimistic in order to continue developing the techniques to determine the transport properties in multicomponent mixtures, taking into account the limited experimental results available for ternary mixtures.

IV. CONCLUSIONS

An analytical method based upon the notion of self-similarity has been developed to enable the determination of molecular diffusion coefficients in ternary mixtures by the SST technique. This method, when combined with a four-dimensional Newton-Raphson scheme, yields the diffusion coefficients very rapidly. The accuracy of these coefficients depends first on the diffusion front not having yet reached the extreme ends of the tubes in our SST experiment, and second on the accuracy of the experimental technique itself. We would claim that both of these conditions are satisfied because the data shown in Figures 4 and 6 yield lines which are almost exactly linear.

In this work, all the diagonal and cross-diagonal molecular diffusion coefficients corresponding to the mixture THN-IBB-*n*C12 with equal mass fraction and at 25 °C have been determined. After comparing these values with the ones shown in the literature, the agreement between the eigenvalues of the diffusion matrix is particularly good and the agreement between the molecular diffusion coefficients is acceptable, especially in the case of the diagonal diffusion coefficients. As can be observed, the cross-diagonal molecular diffusion coefficients are much more sensitive.

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