Determination of the molecular diffusion coefficients in ternary mixtures by the Sliding Symmetric Tubes technique


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ABSTRACT: A new analytical methodology has been developed to determine diagonal and cross-diagonal molecular diffusion coefficients in ternary mixtures by the Sliding Symmetric Tubes technique. The analytical solution is also 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) and at 25ºC. Diagonal and cross-diagonal coefficients are determined for the three possible orders of components, in order to compare the results with the ones available in the literature. A
comparison with published results shows a good agreement for the eigenvalues of the diffusion matrix, and reasonable agreement for the diagonal molecular diffusion coefficients.

1. 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 sector, 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) [5], Open Ended Capillary (OEC) [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 in [13] and [1] the Taylor dispersion principle and the Gouy interferometer were used respectively. In addition, simulations based on molecular dynamics [14] and prediction models [3] 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.

As commented in [16], 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-tetrahydronaphthaline (THN), isobutylbenzene (IBB) and n-dodecane (nC12), with equal mass fraction and at 25ºC has been used. This mixture was selected by the group which takes part in the project DCMIX [17] 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.

This article is organized as follows: in section 2 the methodology, both experimental and analytical, for the determination of the molecular diffusion coefficients by the SST technique is
described. In section 3, experimental results obtained for both binary and ternary mixtures and the discussion about them are presented. Finally, conclusions are shown in section 4.

2. Methodology

2.1. Experimental procedure

The SST technique has been successfully applied in the case of binary mixtures [18-20] and it consists of several sets of tubes (FIG1) which have two positions. In the faced tubes position, the contents of both tubes are in contact and the transport of matter between the tubes arises. By contrast, in the separated tubes position the diffusive process is stopped. All the tubes are filled with the same mixture, but with a slight difference of concentration between the upper and bottom tubes. In an experiment, all the sets of tubes are filled in the separated tubes position and they are introduced into a water bath (see Figure 2) with a temperature control of 0.1 °C, which will maintain them at the same temperature throughout the whole experiment. At the beginning of the experiment all the sets are changed to faced tubes position so that the diffusion may be initiated. From that moment, at various predetermined intervals of time, each tube is changed to the separated tubes position, to preserve their contents for later analysis. At the end of the experiment, the variation of the concentration with time is constructed from the concentrations in each of the tubes (see Figure 3).
Figure 1. A set of Sliding Symmetric Tubes.

Figure 2. Installation of the Sliding Symmetric Tubes technique.
Figure 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.

In order to determine the concentration of each point in a ternary mixture, its density and refractive index are measured by an Anton Paar DMA 5000 vibrating quartz U-tube densimeter with an accuracy of $5 \times 10^{-6}$ g/cm$^3$ and by an Anton Paar RXA 156 refractometer with an accuracy of $2 \times 10^{-5}$ nD, respectively. In the works [21] and [16] is shown that these two properties allow the most accurate determination of the concentration of each component. For the determination of the concentration from the density and the refractive index it is necessary to do a prior calibration where measurements are made of the density and the refractive index of 25 mixtures with concentrations that are close to that of study. Once the calibration coefficients are determined, the concentration of each component, $w_i$, in each point is calculated by the following equations:

$$w_1 = \frac{c'(\rho-a) - c(n_D-a')}{b c' - b c}$$  \hspace{1cm} (1)

$$w_2 = \frac{b(n_D-a') - b r(\rho-a)}{b c' - b r c}$$  \hspace{1cm} (2)

$$w_3 = 1 - w_1 - w_2$$  \hspace{1cm} (3)
where $\rho$ and $n_D$ are the density and the refractive index respectively, and $a$, $a'$, $b$, $b'$, $c$ and $c'$ are the calibration parameters calculated for the mixture (see [15] for details).

2.2. Analytical solution

First, an analytical solution for binary mixtures was developed, which allowed the determination of the molecular diffusion coefficient from the experimental measurements of the variation of the concentration with time. The working equations are the following:

$$\begin{align*}
\omega^{\text{bot}}_m(t) - \frac{\omega^{\text{bot}}_i + \omega^{\text{up}}_i}{2} = \\
\frac{4}{\pi^2} \cdot (\omega^{\text{bot}}_i - \omega^{\text{up}}_i) \cdot \sum_{n=0}^{\infty} e^{-\left(\frac{(n+\frac{1}{2})^2 \pi^2}{L^2} D t\right)} \\
\omega^{\text{up}}_m(t) - \frac{\omega^{\text{bot}}_i + \omega^{\text{up}}_i}{2} = \\
\frac{4}{\pi^2} \cdot (\omega^{\text{up}}_i - \omega^{\text{bot}}_i) \cdot \sum_{n=0}^{\infty} e^{-\left(\frac{(n+\frac{1}{2})^2 \pi^2}{L^2} D t\right)}
\end{align*}$$

(4)

(5)

where $\omega^{\text{up}}_m(t)$ and $\omega^{\text{bot}}_m(t)$ are the mean concentration in the upper tube and bottom tubes respectively, as functions of time; $\omega^{\text{up}}_i$ and $\omega^{\text{bot}}_i$ are the respective initial concentrations, $D$ is the molecular diffusion coefficient and $L$ is the length of the tube.

As may be noted, the formulae given in Eqs. (4) and (5) are linearly dependent and therefore it follows, not surprisingly, that the molecular diffusion coefficient must be the same both in the upper and the lower tubes for binary mixtures.

In [15] an analytical solution for ternary mixtures was obtained by following the same procedure as for the case of binary mixtures. The evolution of the mean concentration of component $j$ was found to be take the following form:

$$\begin{align*}
\phi^{\text{bot}}_j \mid_m(t) - \frac{\phi^{\text{bot}}_j + \phi^{\text{up}}_j}{2} = \\
\frac{4}{\pi^2} \cdot (\phi^{\text{bot}}_j - \phi^{\text{up}}_j) \cdot \sum_{n=0}^{\infty} e^{-\left(\frac{(n+\frac{1}{2})^2 \pi^2}{L^2} \lambda_j t\right)}
\end{align*}$$

(6)
\[ \phi_j^{up} \bigg|_m (t) - \frac{\phi_j^{bot} + \phi_j^{up}}{2} = \]
\[ \frac{4}{\pi^2} \cdot (\phi_j^{up} - \phi_j^{bot}) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \pi^2 \lambda_j t}}{(2n+1)^2} \quad (7) \]
for \( j=1, 2 \) and where \( \phi_j^{up/bot} \bigg|_m (t) \) is the new variable for the mean concentration in the upper and the lower tubes respectively, \( \phi_j^{up/bot} \) is the new variable for the initial concentration in the upper and the lower tubes respectively and the \( \lambda_j \)-values are the eigenvalues of the diffusion matrix.

As may be observed, these equations have become considerably more complicated and in this case there are two linearly independent equations (for each components 1 and 2) and four unknowns (the two diagonal diffusion coefficients and another two cross-diagonal diffusion coefficients). That is why a non-linear fitting had to be applied in order to determine the diffusion coefficients. However, the complexity of the equations made impossible the achievement of reliable results with different fitting methods, as it is detailed in [15].

That difficulty has motivated the development of a new analytical solution which allows the determination of the diffusion coefficients for both binary and ternary mixtures. The new analytical solution is described hereafter; it is illustrated first for binary mixtures and then, it is extended to ternary mixtures.

2.2.a. Analytical solution for binary mixtures

It is intended to solve Fick’s second law,
\[ \frac{\partial w}{\partial t} = D \cdot \frac{\partial^2 w}{\partial x^2} \quad (8) \]
for relatively short times, by which we mean that the developing interface between the upper and lower tubes has not yet reached the far ends of those tubes. In this regime the evolving front satisfies a self-similar solution for which the following changes of variable are required:
\[ \eta = \frac{y}{2\sqrt{Dt}} \]  \hspace{1cm} (9)

\[ \tau = \sqrt{t} \]  \hspace{1cm} (10)

where \( y \) is the vertical variable. Whilst within the self-similar regime the time-derivative may be neglected and therefore the equation for the concentration transforms to:

\[ w'' + 2\eta w' = 0 \]  \hspace{1cm} (11)

where \( w' \) and \( w'' \) are the first and the second derivatives of the concentration with respect to \( \eta \).

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

\[ w \to w_{i \text{bot}} \text{ as } \eta \to -\infty \]

\[ w \to w_{i \text{up}} \text{ as } \eta \to +\infty \]  \hspace{1cm} (12)

where \( w_{i \text{up}} \) and \( w_{i \text{bot}} \) are the initial concentration in the upper and lower tubes respectively. Upon solving the equation (11) the following expression for the concentration is obtained:

\[ w = w_{i \text{up}} + \frac{w_{i \text{bot}} - w_{i \text{up}}}{2} \text{erfc}(\eta) \]  \hspace{1cm} (13)

where \( \text{erfc}(\eta) \) is the well-known complementary error function of \( \eta \) [22].

The mean concentration in each tube is obtained by integrating the solution given in the equation (13) over the length of the tube, and then dividing it by the length of the tube, \( L \).

\[ \frac{1}{L} \int_{0}^{y_{\text{top}}} w \, dy = w_{i \text{up}} + \frac{(w_{i \text{bot}} - w_{i \text{up}})}{2L} \sqrt{\frac{Dt}{\pi}} \]  \hspace{1cm} (14)

Equation (14) shows that the mean concentration varies linearly with \( t^{1/2} \) and therefore, FIG4 represents the 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 25ºC. 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:
$S_{up} = \frac{\left(w_{i,bot}^{up} - w_{i,up}^{up}\right)}{L} \sqrt{\frac{D}{\pi}} \quad (15)$

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.

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

2.2.b. 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 eigensolutions as will be seen. For ternary mixtures Fick’s second law may be written as follows:

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

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

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:

$$\eta = \frac{y}{z \sqrt{t}} \quad (18)$$
\( \tau = \sqrt{t} \) \hfill (19)

\( z = \alpha \eta \) \hfill (20)

where \( \alpha \) is an eigenvalue which is to be found. Under steady-state conditions the following equations are obtained for the concentrations of the components 1 and 2:

\[ D_{11} \alpha^2 w_1'' + 2zw_1' + D_{12} \alpha^2 w_2'' = 0 \] \hfill (21)

\[ D_{21} \alpha^2 w_1'' + D_{22} \alpha^2 w_2'' + 2zw_2' = 0 \] \hfill (22)

where primes 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:

\( w_1 \to w_{11}^{bot} \) and \( w_2 \to w_{12}^{bot} \) as \( \eta \to -\infty \)

\( w_1 \to w_{11}^{up} \) and \( w_2 \to w_{12}^{up} \) as \( \eta \to +\infty \) \hfill (23)

where \( w_{11}^{up}, w_{11}^{bot}, w_{12}^{up} \) and \( w_{12}^{bot} \) are the initial conditions of the components 1 and 2 in the upper and lower tubes respectively.

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

\[
w_1 = A \text{erfc}(z_1) + B \text{erfc}(z_2) + w_{11}^{up} \] \hfill (24)

\[
w_2 = A \left( \frac{1-D_{11} \alpha_1^2}{D_{12} \alpha_1^2} \right) \text{erfc}(z_1) + \]

\[
B \left( \frac{1-D_{11} \alpha_2^2}{D_{12} \alpha_2^2} \right) \text{erfc}(z_2) + w_{12}^{up} \] \hfill (25)

where the constants \( A \) and \( B \) are functions of the diffusion coefficients and the initial concentrations of the components 1 and 2 in the upper and the lower tubes:

\[
A = \frac{D_{12} \alpha_2^2(1-D_{12} \alpha_1^2) - D_{11} \alpha_1^2 w_{12}^{bot} - w_{12}^{up}}{2(\alpha_2^2-\alpha_1^2)} \] \hfill (26)

\[
B = \frac{D_{12} \alpha_2^2(1-D_{12} \alpha_1^2) - D_{11} \alpha_1^2 w_{12}^{bot} - w_{12}^{up}}{2(\alpha_1^2-\alpha_2^2)} \] \hfill (27)

and the values \( \alpha_1 \) and \( \alpha_2 \) which are proportional to the eigenvalues of the diffusivity matrix, are given by:
As with 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.

\[
\frac{1}{L} \int_0^{y_{top}} w_1 \, dy = w_{12}^{up} + \frac{2}{L} \sqrt{\frac{\pi}{\alpha_1 + \alpha_2}}
\]

\[
\frac{1}{L} \int_0^{y_{top}} w_2 \, dy = w_{12}^{up} + \frac{2}{L} \sqrt{\frac{\pi}{\alpha_1 (\frac{1-D_{11} \alpha_1^2}{D_{12} \alpha_2^2}) + \frac{B}{\alpha_2 (\frac{1-D_{11} \alpha_1^2}{D_{12} \alpha_2^2})}}
\]

In the case of ternary mixtures, the variation of the concentration of each component with the square root of time is also linear. Equations (30) and (31) may be manipulated as before to give the slope of the line corresponding to each component:

\[
S_1 = \frac{2}{L \sqrt{\pi}} \left( \frac{A}{\alpha_1} + \frac{B}{\alpha_2} \right)
\]

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

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. (32) and (33) 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. Therefore the Newton-Raphson method has been employed with the help of the program *Matlab*.

3. Results and discussion

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

3.1. Binary mixtures

In previous works, such as [18-20], the validity of the SST technique and the first analytical solution (given by Eqs. (4) and (5)) for the determination of the molecular diffusion coefficients in binary mixtures has 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 first 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 25ºC, and for the mixture water-isopropanol for many different mass concentrations of water and at 25ºC.

![Figure 5](image.png)

**Figure 5.** Comparison of the results obtained by the equations (4) and (5), and the equation (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 at 25ºC.

The good agreement between the results obtained by both methods proves the validity of the new analytical solution developed in this work, in the case of binary mixtures.

3.2. Ternary mixtures

In the work [15] the determination of the diagonal and cross-diagonal molecular diffusion coefficients using 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 which do 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 fraction and at 25ºC 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 experiments where the initial concentrations are different. Table 1 shows the initial concentrations of each component in the two experiments used in this case.

**Table 1.** Initial concentrations of each component in the upper and the bottom tubes, in the two experiments carried out in this work, at 25ºC.

<table>
<thead>
<tr>
<th>Component</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>w (THN) up</td>
<td>0.3033</td>
<td>0.3033</td>
</tr>
<tr>
<td>w (THN) bot</td>
<td>0.3633</td>
<td>0.3633</td>
</tr>
</tbody>
</table>
As for the case of binary mixtures, the variation of the concentration with the square root of time forms a linear regression. Figure 6 shows experimental results for the mixture THN-IBB-\( n\)C12 with equal mass fraction and 25ºC, corresponding to the experiment 1 of the Table 1.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>w (IBB) up</td>
<td>0.3433</td>
<td>0.3333</td>
</tr>
<tr>
<td>w (IBB) bot</td>
<td>0.3233</td>
<td>0.3333</td>
</tr>
<tr>
<td>w (C12) up</td>
<td>0.3533</td>
<td>0.3633</td>
</tr>
<tr>
<td>w (C12) bot</td>
<td>0.3133</td>
<td>0.3033</td>
</tr>
</tbody>
</table>

**Figure 6.** Variation of the concentration with the square root of time for the components THN, IBB and \( n\)C12 at 25ºC, obtained in the upper tube of the SST technique.

Before showing the obtained results and comparing them to the results available in the literature, it is necessary to pay attention to the order of the components in a ternary mixture. The fact is that depending on which two components (\(w_1\) and \(w_2\)) are taken into account in the flux equations (34) and (35), the four diagonal and cross-diagonal molecular diffusion coefficients determined (\(D_{11}, D_{12}, D_{21}\) and \(D_{22}\)) are different, because, logically, they correspond to different components of the mixture.
\begin{align*}
J_1 &= -\rho (D_{11} \nabla w_1 + D_{12} \nabla w + D'_{T,1} \nabla T) \\
J_2 &= -\rho (D_{21} \nabla w_1 + D_{22} \nabla w + D'_{T,2} \nabla T)
\end{align*}

That is why special care needs to be taken when results of different scientific groups are compared. Due to the analysis method used in this laboratory, considering the components with higher and lower density in the flux equations allows the more accurate results; therefore those components are the ones generally chosen as \( w_1 \) and \( w_2 \). However, in order to compare the obtained results with the ones available in the literature, molecular diffusion coefficients for the three possible orders of components have been experimentally determined. Table 2 shows the diagonal and cross-diagonal molecular diffusion coefficients determined in this work for the three possible orders of components in the mixture.

**Table 2.** Molecular diffusion coefficients determined in this work for the mixture THN-IBB-\( n \)C12 with equal mass fraction and at 25ºC for the three possible order of components.

<table>
<thead>
<tr>
<th>Order of components</th>
<th>( D'_{11} \times 10^{-10} ) m(^2)/s</th>
<th>( D'_{12} \times 10^{-10} ) m(^2)/s</th>
<th>( D'_{21} \times 10^{-10} ) m(^2)/s</th>
<th>( D'_{22} \times 10^{-10} ) m(^2)/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>THN-IBB-( n )C12</td>
<td>6.16</td>
<td>-4.61</td>
<td>0.37</td>
<td>11.40</td>
</tr>
<tr>
<td>THN-( n )C12-IBB</td>
<td>11.30</td>
<td>5.08</td>
<td>0.14</td>
<td>6.65</td>
</tr>
<tr>
<td>( n )C12-IBB-THN</td>
<td>6.54</td>
<td>-0.51</td>
<td>-0.37</td>
<td>11.06</td>
</tr>
</tbody>
</table>

In the three cases the molecular diffusion coefficients satisfy the restrictions detailed in [23].

The comparison between the results obtained in this work and the ones of the two works of the literature which offer results for this mixture is shown below. In [10] the molecular diffusion coefficients have been determined by the two colour optical beam deflection technique, considering \( n \)C12 and IBB as components \( w_1 \) and \( w_2 \) respectively; in [11] the diffusion
coefficients have been determined by interferometry and THN and IBB have been considered as components \( w_1 \) and \( w_2 \) respectively.

Table 3 shows the eigenvalues of the diffusion matrix determined in this work (rows 2, 3 and 4) and the ones determined in the works [10] (row 5) and [11] (row 6). The second column indicates the order of the components that has 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.

**Table 3.** Comparison between the eigenvalues of the diffusion matrix obtained in this work and the results of the literature.

<table>
<thead>
<tr>
<th>Data source</th>
<th>Order of components</th>
<th>( \bar{D}_1 ) ( 10^{10} ) m(^2)/s</th>
<th>( \bar{D}_2 ) ( 10^{10} ) m(^2)/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>THN-IBB-( n )C(_{12} )</td>
<td>6.51</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>THN-( n )C(_{12} )-IBB</td>
<td>6.49</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>( n )C(_{12} )-IBB-THN</td>
<td>6.50</td>
<td>11.11</td>
</tr>
<tr>
<td>Königer et al. [10]</td>
<td>( n )C(_{12} )-IBB-THN</td>
<td>6.81</td>
<td>10.99</td>
</tr>
<tr>
<td>Mialdun et al. [11]</td>
<td>THN-IBB-( n )C(_{12} )</td>
<td>7.26</td>
<td>11.23</td>
</tr>
</tbody>
</table>

As can be observed, the agreement between the determined eigenvalues is reasonable, obtaining differences around 5% and 1% in comparison to [10] and differences around 12% and 1% in comparison to [11].

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 the Eqs. (A8)-(A11) of reference [10] has been applied to the results of this work and to the results of the literature, in the cases needed.
Table 4 shows the results obtained in the case of considering the order of components THN-IBB-nC12. Table 5 shows the results obtained when the order of components considered is nC12-IBB-THN. Finally, Table 6 shows the results obtained in the case of considering the order of components THN-nC12-IBB.

**Table 4.** Comparison of the diffusion coefficients in the ternary mixture THN-IBB-nC12 with equal mass fraction and at 25ºC, considering THN and IBB as components $w_1$ and $w_2$ respectively.

<table>
<thead>
<tr>
<th>Data source</th>
<th>Order of components</th>
<th>$D_{11} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{12} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{21} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{22} \times 10^{-10}$ m$^2$/s</th>
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<tbody>
<tr>
<td>Present study</td>
<td>THN-IBB-nC12</td>
<td>6.16</td>
<td>-4.61</td>
<td>0.37</td>
<td>11.40</td>
</tr>
<tr>
<td>Present study*</td>
<td></td>
<td>6.22</td>
<td>-5.08</td>
<td>0.28</td>
<td>11.73</td>
</tr>
<tr>
<td>Königier et al. [10]*</td>
<td></td>
<td>5.62</td>
<td>-5.91</td>
<td>1.08</td>
<td>12.18</td>
</tr>
<tr>
<td>Mialdun et al. [11]</td>
<td></td>
<td>6.92</td>
<td>1.06</td>
<td>-1.37</td>
<td>11.57</td>
</tr>
</tbody>
</table>

* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in [10]).

**Table 5.** Comparison of the diffusion coefficients in the ternary mixture THN-IBB-nC12 with equal mass fraction and at 25ºC, considering nC12 and IBB as components $w_1$ and $w_2$ respectively.

<table>
<thead>
<tr>
<th>Data source</th>
<th>Order of components</th>
<th>$D_{11} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{12} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{21} \times 10^{-10}$ m$^2$/s</th>
<th>$D_{22} \times 10^{-10}$ m$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>nC12-IBB-THN</td>
<td>6.54</td>
<td>-0.51</td>
<td>-0.37</td>
<td>11.06</td>
</tr>
<tr>
<td>Present study*</td>
<td></td>
<td>6.51</td>
<td>-0.14</td>
<td>-0.28</td>
<td>11.14</td>
</tr>
<tr>
<td>Königier et al. [10]</td>
<td></td>
<td>6.70</td>
<td>0.43</td>
<td>-1.08</td>
<td>11.10</td>
</tr>
<tr>
<td>Mialdun et al. [11]*</td>
<td></td>
<td>5.55</td>
<td>-7.08</td>
<td>1.37</td>
<td>12.94</td>
</tr>
</tbody>
</table>

* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in [10]).
Table 6. Comparison of the diffusion coefficients in the ternary mixture THN-IBB-\(n\)C12 with equal mass fraction and at 25ºC, considering THN and \(n\)C12 as components \(w_1\) and \(w_2\) respectively.

<table>
<thead>
<tr>
<th>Data source</th>
<th>Order of components</th>
<th>(D_{11}) (10^{-10}) m(^2)/s</th>
<th>(D_{12}) (10^{-10}) m(^2)/s</th>
<th>(D_{23}) (10^{-10}) m(^2)/s</th>
<th>(D_{22}) (10^{-10}) m(^2)/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>THN-(n)C12-IBB</td>
<td>11.30</td>
<td>5.08</td>
<td>0.14</td>
<td>6.65</td>
</tr>
<tr>
<td>Königler et al. [10]*</td>
<td>THN-(n)C12-IBB</td>
<td>11.53</td>
<td>5.91</td>
<td>-0.43</td>
<td>6.27</td>
</tr>
<tr>
<td>Mialdun et al. [11]*</td>
<td></td>
<td>5.86</td>
<td>-1.06</td>
<td>7.08</td>
<td>12.63</td>
</tr>
</tbody>
</table>

* Data has been transformed for the same order of components (Eqs. (A8)-(A11) in [10]).

As may be seen in Tables 4-6, 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 [10]. In the case of the cross-diagonal diffusion coefficients the differences are bigger, appearing in some cases even a disagreement in the sign.

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 [16]. In [24] this scientific team published the thermodiffusion coefficients for the mixture studied in this work determined by the thermogravitational technique. 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 25ºC. Table 7 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 technique in [10] (row 5).
Table 7. Comparison of the Soret coefficients in the ternary mixture THN-IBB-\(n\)C12 with equal mass fraction and at 25ºC

<table>
<thead>
<tr>
<th>Data source</th>
<th>Order of components</th>
<th>(S_{THN}^R) (10^{-3}) K(^{-1})</th>
<th>(S_{IBB}^R) (10^{-3}) K(^{-1})</th>
<th>(S_{nC12}^R) (10^{-3}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>THN-IBB-(n)C12</td>
<td>1.83</td>
<td>0.05</td>
<td>-1.88</td>
</tr>
<tr>
<td></td>
<td>THN-(n)C12-IBB</td>
<td>1.82</td>
<td>0.07</td>
<td>-1.89</td>
</tr>
<tr>
<td></td>
<td>(n)C12-IBB-THN</td>
<td>1.83</td>
<td>0.05</td>
<td>-1.88</td>
</tr>
<tr>
<td>König et al. [10]</td>
<td>(n)C12-IBB-THN</td>
<td>2.11</td>
<td>-0.96</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

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 7). The agreement between the results obtained in this work and the ones shown in [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.

4. Conclusions

The analytical solution developed in this work to determine the molecular diffusion coefficients in ternary mixtures, combined with the SST technique makes possible the determination of the diffusion coefficients.

In this work the all diagonal and cross-diagonal molecular diffusion coefficients corresponding to the mixture THN-IBB-\(n\)C12 with equal mass fraction and at 25ºC have been determined. After comparing these values to the ones shown in the literature, the agreement between the eigenvalues of the diffusion matrix is considerably 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.

In order to make easier the comparison between the results obtained by different scientific groups, it would be interesting to consider always the same components in the flux equations. For example, in decreasing order of density as was suggested in [20]. Anyway, the transformation described in [10], always can be applied.

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REFERENCES


[17] Diffusion Coefficient Measurements in ternary Mixtures DCMIX-NCR-00022-QS.


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ABBREVIATIONS

Hay que poner?

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