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Remarks on the analysis method for determining diffusion coefficient in ternary mixtures

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ABSTRACT

The objective of this work is the determination of diagonal and cross-diagonal molecular diffusion coefficients in a ternary mixture, using the 'Sliding Symmetric Tubes' (SST) technique. The analyzed mixture consists of two aromatics and one normal alkane (tetrahydronaphthalene–dodecane–isobutylbenzene) with an equal mass fraction for all components (1:1:1) at 25 °C. The analytical solution corresponding to the SST technique has been successfully derived. The different fitting procedures were utilized by two scientific teams to subtract diffusion coefficients from the experimentally measured time-dependent concentration field. None of the attempts provided reliable results for the data from a single experiment. The "simplex"-based methods display reasonable results assuming that cross-diagonal coefficients are close to zero, i.e. quasi-binary and diluted mixtures. The results obtained by "trust region method" are satisfactory if the initial guess is good. To achieve better results, it is necessary to increase the number of experimental data.

1. Introduction

A concentration gradient within a liquid mixture generates a transport of matter from the zones of higher concentration, to the ones of lower concentration. This phenomenon is known as molecular diffusion and it has generated a big interest since its discovery in the nineteenth century, when it was studied in order to understand the atom's behavior. In 1855 Fick [1] established the first quantitative relation for the molecular diffusion phenomenon, known as Fick's law. Since then, the interest on this phenomenon has increased, discovering the influence it has in many fields, such as medicine or physiology [2].

Due to this interest, a lot of new experimental techniques designed for the determination of the molecular diffusion coefficient have been developed. These are, for example, techniques that employ the Taylor dispersion principle [3], or Open Ended Capillary technique (OEC) [4] or Thermal Forced Rayleigh Scattering (TDFRS) [5]. Other different techniques used for the determination of the molecular diffusion coefficient can be found in the literature [2,6–9]. The Sliding Symmetric Tubes technique was developed in order to make up for some limitations of the OEC technique, such as the problem of the evaporations or the volume of fluid needed for each experiment [10].

Molecular diffusion in multicomponent mixtures has a very important role in a lot of natural and industrial processes. However, although there are plenty of experimental data in binary mixtures, in the case of multicomponent mixtures the

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available information, both theoretical and experimental, is limited [11]. The existence of cross-diagonal diffusion coefficients makes their determination difficult already in ternary mixtures.

The main objective of this work is to analyze the results obtained by different fitting procedures done in order to determinate the diagonal and cross-diagonal molecular diffusion coefficients from the measurements of a concentration variation with time by the SST technique.

This article is organized as follows: in Section 2, the SST technique is presented; the details of the elaboration of the analytical solution for ternary mixtures and the description of the experimental method are given. In Section 3, the experimental results are analyzed and, particularly, the dependence of the determined molecular diffusion coefficients D_{ij} $(i, j = 1, 2)$ on fitting procedure is discussed. Finally, conclusions are drawn in Section 4.

2. Sliding Symmetric Tubes technique

2.1. Technique description

In the SST technique, several sets of two identical vertical tubes can be used. Each set has two positions: 'faced tubes' and 'separated tubes' [12]. In 'faced tubes' position the mixture of both tubes is in contact, allowing the transport of matter; whereas in 'separated tubes' position, the transport of matter is stopped. At the beginning of the experiment, the studied mixture is introduced in each tube, with a slight concentration difference. The denser mixture is introduced in the bottom tube, and the upper tube is filled with the less dense mixture in order to avoid the convective instability.

This technique was validated in previous works, [13], using 5 binary mixtures: the three binary mixtures composed by 1,2,3,4-tetrahydronaphthalene (THN), dodecane (nC12), and isobutylbenzene (IBB) at 25 °C and 50 wt%, used in a benchmark test [14], and the binary mixtures: water/ethanol at 25 °C and 60.88 wt% water and toluene/n-hexane at 25 °C and 51.67 wt% toluene, which have been extensively studied in the literature [15–19]. In general, the differences with the published data are below 3%.

2.2. Analytical solution

Assuming Fick's second law in one dimension (z: vertical direction), the following system of equations for a ternary mixture is obtained, where the corresponding matrix to the diagonal and cross-diagonal molecular diffusion coefficients appears.

$$\frac{\partial}{\partial t}\begin{Bmatrix} w_1 \\ w_2 \end{Bmatrix} = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \cdot \frac{\partial^2}{\partial z^2}\begin{Bmatrix} w_1 \\ w_2 \end{Bmatrix} \to \begin{cases} \frac{\partial w_1}{\partial t} = D_{11} \cdot \frac{\partial^2 w_1}{\partial z^2} + D_{12} \cdot \frac{\partial^2 w_2}{\partial z^2} \\ \frac{\partial w_2}{\partial t} = D_{21} \cdot \frac{\partial^2 w_1}{\partial z^2} + D_{22} \cdot \frac{\partial^2 w_2}{\partial z^2} \end{cases} \tag{1}$$

where w_1 and w_2 are the concentrations of the component 1 and the component 2, respectively, and D_{11}, D_{22}, D_{12}, and D_{21} are the diagonal and cross-diagonal molecular diffusion coefficients.

The boundary conditions in this case are:

$$\overline{w}(z, 0) = f(z) = \begin{cases} w_i^{\text{bot}} & 0 \leqslant z < L \\ w_i^{\text{up}} & L < z \leqslant 2L \end{cases} \tag{2}$$

$$\left.\frac{\partial w_i}{\partial z}\right|_{z=0,2L} = 0 \quad \forall t \tag{3}$$

where w_i^{up} and w_i^{bot} are the initial mass fractions in the upper and the bottom tubes, respectively.

As has been done in the case of the OEC technique [20], the system (1) can be solved diagonalizing the diffusion matrix $\overline{\overline{D}}$ in order to uncouple the system into two equations. In this case, obtained eigenvalues and eigenvectors matrix are given by:

$$\lambda_1 = \frac{D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4 \cdot D_{12} \cdot D_{21}}}{2} \tag{4}$$

$$\lambda_2 = \frac{D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4 \cdot D_{12} \cdot D_{21}}}{2} \tag{5}$$

$$\overline{\overline{P}} = \begin{bmatrix} 1 & \frac{D_{12}}{\lambda_2 - D_{11}} \\ \frac{\lambda_1 - D_{11}}{D_{12}} & 1 \end{bmatrix} \tag{6}$$

The diagonalization allows us to define a new concentration variable:

$$\overline{\phi} = \overline{\overline{P}}^{-1} \cdot \overline{w} \tag{7}$$

It results in a new problem where the equations are uncoupled and where there are new initial and boundary conditions:

$$\begin{Bmatrix} \frac{\partial \phi_1}{\partial t} \\ \frac{\partial \phi_2}{\partial t} \end{Bmatrix} = [D_d] \cdot \begin{Bmatrix} \frac{\partial^2 \phi_1}{\partial z^2} \\ \frac{\partial^2 \phi_2}{\partial z^2} \end{Bmatrix} \tag{8}$$

$$\bar{\phi}_i(z,0) = \begin{cases} \bar{\bar{P}}^{-1} \cdot \overline{w_l^{\text{bot}}} & 0 < z < L \\ \bar{\bar{P}}^{-1} \cdot \overline{w_l^{\text{up}}} & L < z < 2L \end{cases} \tag{9}$$

$$\left.\frac{\partial \bar{\phi}_i}{\partial z}\right|_{z=0,2L} = 0 \quad \forall t \tag{10}$$

The equations solved by the separation of variables method, as it was done in the case of binary mixtures [12], yield to the following equations for the mean concentration of the component 1 and the component 2, in the upper tube and the bottom tube ($\emptyset_i^{\text{up/bot}}|_{\text{m}}$):

$$\emptyset_1^{\text{bot}}\big|_{\text{m}}(t) - \frac{\phi_{1i}^{\text{bot}} + \phi_{1i}^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(\phi_{1i}^{\text{bot}} - \phi_{1i}^{\text{up}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_1 \cdot t}}{(2n+1)^2} \tag{11}$$

$$\emptyset_1^{\text{up}}\big|_{\text{m}}(t) - \frac{\phi_{1i}^{\text{bot}} + \phi_{1i}^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(\phi_{1i}^{\text{up}} - \phi_{1i}^{\text{bot}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_1 \cdot t}}{(2n+1)^2} \tag{12}$$

$$\emptyset_2^{\text{bot}}\big|_{\text{m}}(t) - \frac{\phi_{2i}^{\text{bot}} + \phi_{2i}^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(\phi_{2i}^{\text{bot}} - \phi_{2i}^{\text{up}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_2 \cdot t}}{(2n+1)^2} \tag{13}$$

$$\emptyset_2^{\text{up}}\big|_{\text{m}}(t) - \frac{\phi_{2i}^{\text{bot}} + \phi_{2i}^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(\phi_{2i}^{\text{up}} - \phi_{2i}^{\text{bot}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot \lambda_2 \cdot t}}{(2n+1)^2} \tag{14}$$

In order to check the obtained equations, the transition from the ternary to binary mixture is applied in Eqs. (13), (14). For that, it is taken into account that in the case of binary mixtures, the concentration of only one of the components is considered, and there exists only one molecular diffusion coefficient D.

$$D_{11} = D_{22} = D \tag{15}$$

$$D_{12} = D_{21} = 0 \tag{16}$$

The eigenvalues (4) and (5) of the matrix are as follows:

$$\lambda_1 = \frac{D + D + 0}{2} = D \tag{17}$$

$$\lambda_2 = \frac{D + D - 0}{2} = D \tag{18}$$

Substituting these values in Eqs. (11)–(14), the following expressions are obtained:

$$w_l^{\text{bot}}\big|_{\text{m}}(t) - \frac{w_i^{\text{bot}} + w_i^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(w_i^{\text{bot}} - w_i^{\text{up}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot D \cdot t}}{(2n+1)^2} \tag{19}$$

$$w_l^{\text{up}}\big|_{\text{m}}(t) - \frac{w_i^{\text{bot}} + w_i^{\text{up}}}{2} = \frac{4}{\pi^2} \cdot \left(w_i^{\text{up}} - w_i^{\text{bot}}\right) \cdot \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})^2 \cdot \frac{\pi^2}{L^2} \cdot D \cdot t}}{(2n+1)^2} \tag{20}$$

The obtained solution is the same as the one in the case of binary mixtures [12], so it can be corroborated that the solution calculated is correct.

Moreover, it should be added that there are some restrictions [11] that diagonal and cross-diagonal molecular diffusion coefficients must satisfy, and which can also be used for validation of the obtained results [11]. According to Taylor and Krishna [6], the restrictions are the following:

The diagonal diffusion coefficients are positive:

$$\begin{aligned} &D_{11} > 0 \\ &D_{22} > 0 \end{aligned} \tag{21}$$

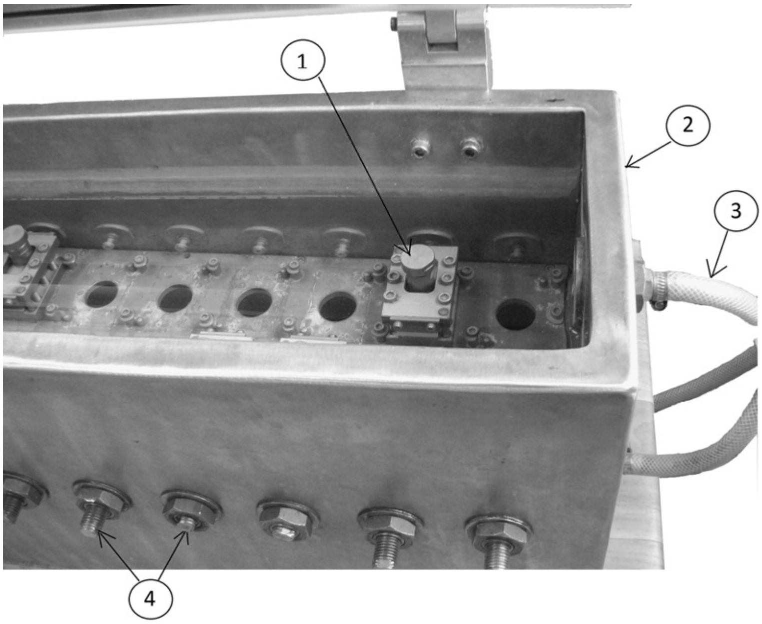


Fig. 1. Installation of the SST technique. (1) Sets of the SST technique; (2) water bath; (3) water circuit for temperature control; (4) screws used to make the tubes slide from one position to the other.

The determinant $\overline{\overline{D}}$ of the diffusion matrix is positive:

$$D_{11}D_{22} - D_{12}D_{21} > 0 \tag{22}$$

The eigenvalues (4) and (5) are real:

$$(D_{11} - D_{22})^2 + 4 \cdot D_{12} \cdot D_{21} \geqslant 0 \tag{23}$$

2.3. Equipment and procedure

The SST equipment, designed and constructed in Mondragon Goi Eskola Politeknikoa has been used to determine the molecular diffusion coefficient [10].

In an experimental run, 10 sets of tubes are filled and put in the 'separated tubes' position. Then, all the sets are placed in the water bath, described in Fig. 1, so that the mixtures are maintained at the working temperature during all the experiment. The temperature of the water in the bath is controlled by a thermostatic bath with a temperature control of 0.1 °C. To ensure that the mixture is at the working temperature, the sets are placed in the water bath 48 hours prior to the experiment in the 'separated tubes' configuration.

Once the mixture has reached the working temperature, all the sets are changed to 'faced tubes' position by the external screws. Since this moment, at prescribed time intervals, each set is changed to 'separated tubes' position. After stopping the molecular diffusion process, the concentration of each tube is analyzed. Therefore, at the end of the experiment, the variation of the mean concentration with time in each tube is obtained.

To determine the concentration in each point, the density and the refractive index of the mixture were measured by an *Anton Paar DMA 5000* vibrating quartz U-tube densimeter with an accuracy of 5×10^{-6} g/cm^3 and by an *Anton Paar RXA* 156 refractometer with an accuracy of 2×10^{-5} nD, respectively. From the density and the refractive index, the concentration of each component is obtained by these equations:

$$w_1 = \frac{c'(\rho - a) - c(n_D - a')}{bc' - b'c} \tag{24}$$

$$w_2 = \frac{b(n_D - a') - b'(\rho - a)}{bc' - b'c} \tag{25}$$

$$w_3 = 1 - w_1 - w_2 \tag{26}$$

where ρ and n_D are the density and refractive index, respectively, and a, a', b, b', c and c' are the calibration parameters obtained for each mixture. Those parameters were obtained from calibration planes. In order to create these planes (Fig. 2), 25 mixtures with concentrations around the studied one were analyzed.

Measurements of density and refractive index allow us to determine the parameters which define the calibration planes. In the case of the mixture analyzed in this work, the calibration parameters were those shown in Table 1.

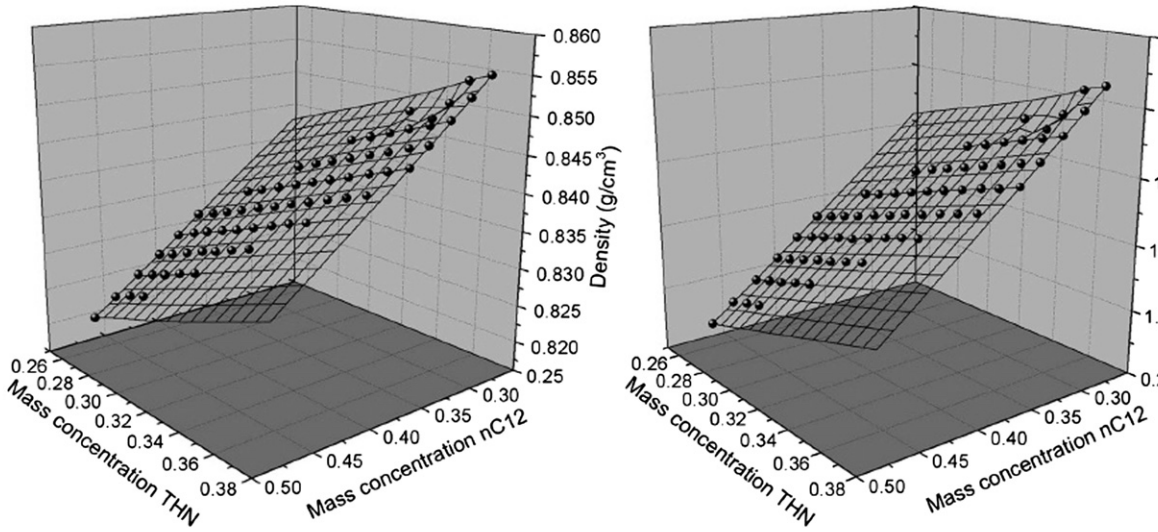


Fig. 2. Calibration planes for THN–*n*C12–IBB mixture around the point with mass fraction (1:1:1) at 25 °C.

Table 1
Calibration parameters for THN–*n*C12–IBB mixture with mass fraction of (1:1:1), and at 25 °C.

a	0.848055	*a*′	1.483118
b	0.101957	*b*′	0.047281
c	−0.115442	*c*′	−0.071592

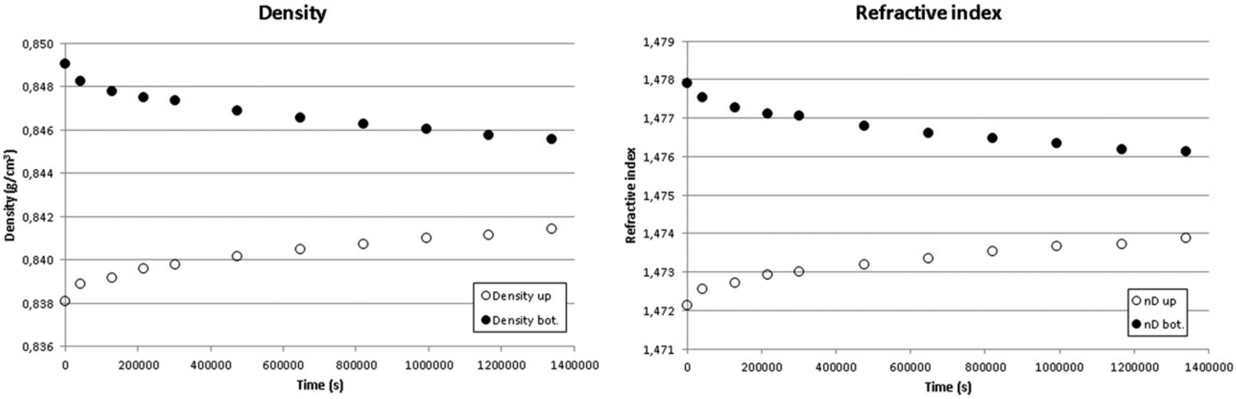


Fig. 3. Density and refractive index variation in the upper and the bottom tubes for THN–*n*C12–IBB mixture with mass fraction of (1:1:1) at 25 °C.

3. Results and discussion

3.1. Experimental results

The mixture used in this study was formed by THN, *n*C12 and IBB at 1/3 mass fraction of each component. All the components were purchased from Merck with purity better than 99% in the case of *n*C12 and better than 98% in the case of THN and IBB. The studied mixtures were prepared by weight using a *Gram VXI-310* digital scale with a precision of 1×10^{-4} g, introducing them in decreasing order of volatility. After the preparation, density and refractive index were measured in order to confirm, using the calibration, that the mixture had the intended composition.

During this study, THN was taken as component 1 and *n*C12 was taken as component 2. The mass fraction of the third component, IBB, is obtained from Eq. (26). The variations of density and refractive index with respect to time were determined and the corresponding results for the components 1 and 2 in the upper and bottom tubes are shown in Fig. 3.

Using Eqs. (24) and (25) and the experimental data, the variation of the concentration of each component with time was determined, see Fig. 4.

The initial concentrations of each component in this experiment are displayed in Table 2.

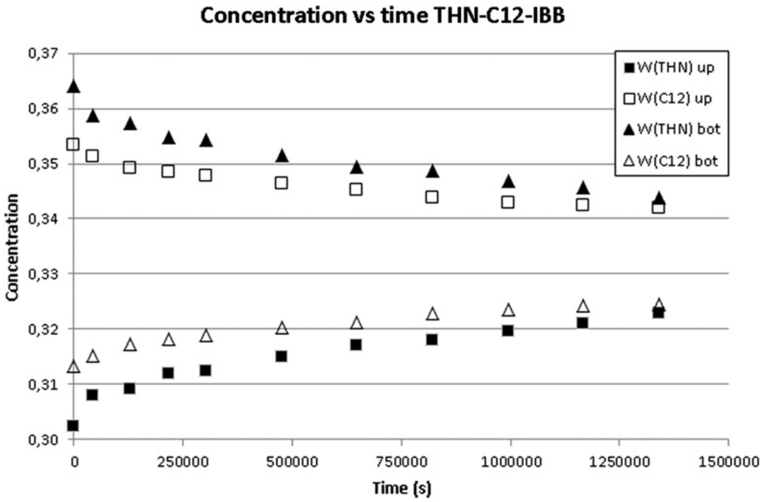


Fig. 4. Variation of the concentration of the components 1 and 2 with time, for THN–nC12–IBB mixture with mass fraction of (1:1:1) at 25 °C.

Table 2
Initial concentrations of each component in the experiment.

	THN	nC12	IBB
Upper tube	0.3033	0.3533	0.3433
Bottom tube	0.3633	0.3133	0.3233

3.2. *Fitting*

Direct determination of the four diffusion coefficients from the experimental results is impossible because a system of two equations contains four unknowns. Four-parameter fittings are not always stable. Because of that, the effect of the fitting procedure on the values of the determined diffusion coefficients is analyzed. Two teams, one from the University of Mondragon, and another from the University of Brussels have tested different fitting procedures.

3.2.1. *Fitting tests by "fminsearch" using simultaneously four sets of concentrations*

The obtained experimental results provide information about the variation of the concentration of each component with time, $\overline{w}(t)$. The four analytical expressions (11)–(14) determine the function $\overline{\phi}$, which is linked with concentration $\overline{w}(t)$ via matrix $\overline{\overline{P}}$, see Eq. (6). Before applying a transformation from $\overline{\phi}$ to $\overline{w}$ the number of terms of the summation that it was going to be used in Eqs. (11)–(14) should be fixed. In the literature there exist works where only the first term of the series is taken, that corresponds to $n = 0$ [4,11,20]. This approach is correct only if the rest of the terms of the summation are insignificant. Here large number of terms ($n = 100$) were used in order to take into account all experimental points from the beginning of the experiment. The fitting procedure searches diffusion coefficients which correspond to minimal difference between analytical and experimental time-dependent profiles.

In this section, a simultaneous fitting of four sets of concentrations (components 1 and 2 in the upper and the bottom tubes) is discussed. The fitting procedure needs an initial guess from which the program starts searching the solution. The fitting was undertaken by the function "*fminsearch*" of the *MATLAB* software [21] and its results are shown in Fig. 5. The used starting data were: $D_{11} = D_{12} = D_{21} = D_{22} = 1 \times 10^{-9}$.

The fitting procedure converges to a solution which satisfied to the restrictions imposed on diffusion coefficients in ternary mixtures (Eqs. (21)–(23)). The obtained coefficients are given in Table 3 (first row), where THN as component 1 and nC12 as component 2.

Several tests were done in order to make sure that the fitting was correct. First, the fitting was repeated with different initial guesses, in order to check that the solution converges to a global minimum instead of a local one. In all cases, the fitting converges to the same set of diffusion coefficients.

Second, reproducibility of the fitting was verified. From the obtained solution, the new points of $w(t)$ that correspond to the obtained diffusion values were calculated. Then, the fitting was applied again. It was expected that the solution obtained would be the same; however, although the obtained curve in the second case coincided with the initial curve (Fig. 6), the values of the diffusion coefficients, especially the ones with lower order, changed noticeably (see first two rows in Table 3).

Although the fitting was converging, it seems that the solution for the fitting is not unique. In the case of D_{11} and D_{12} the variation is small and reasonable; however, in the case of D_{21} and D_{22} the difference is considerable. In addition, D_{11}

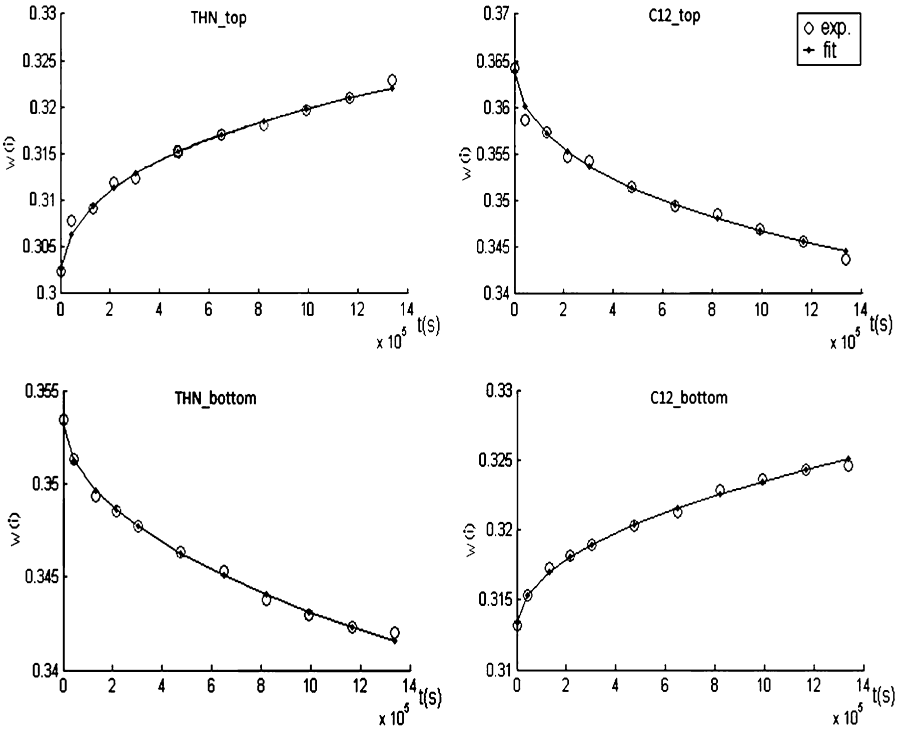


Fig. 5. Simultaneous fitting of four concentrations: components 1 and 2 in the upper and the bottom tubes for THN–*n*C12–IBB mixture with mass fraction of (1:1:1) at 25 °C.

Table 3
Diffusion coefficients obtained by the different fitting procedures for THN–*n*C12–IBB.

Fitting procedure		D_{11} 10^{-9} (m^2/s)	D_{12} 10^{-9} (m^2/s)	D_{21} 10^{-9} (m^2/s)	D_{22} 10^{-9} (m^2/s)	λ_1 10^{-10} (m^2/s)	λ_2 10^{-10} (m^2/s)
"fminsearch"	original fit	6.693	8.135	−0.348	0.252		
	repeated (2nd)	6.638	8.051	−0.213	0.440		
Simplex	2-parameter fit	0.947	10^{-16}	10^{-16}	0.737	7.37	9.47
Trust region method	4-parameter fit	0.982	0.047	∼0	0.74	7.4	9.82
OBD, Ref. [23]						6.81	10.99

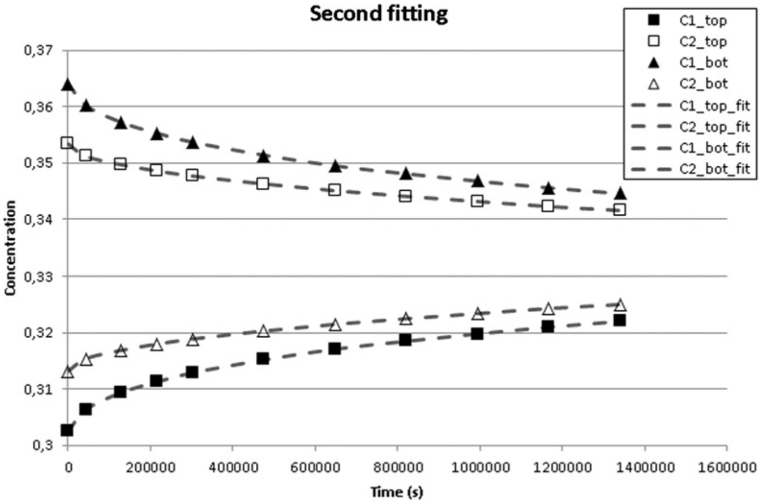
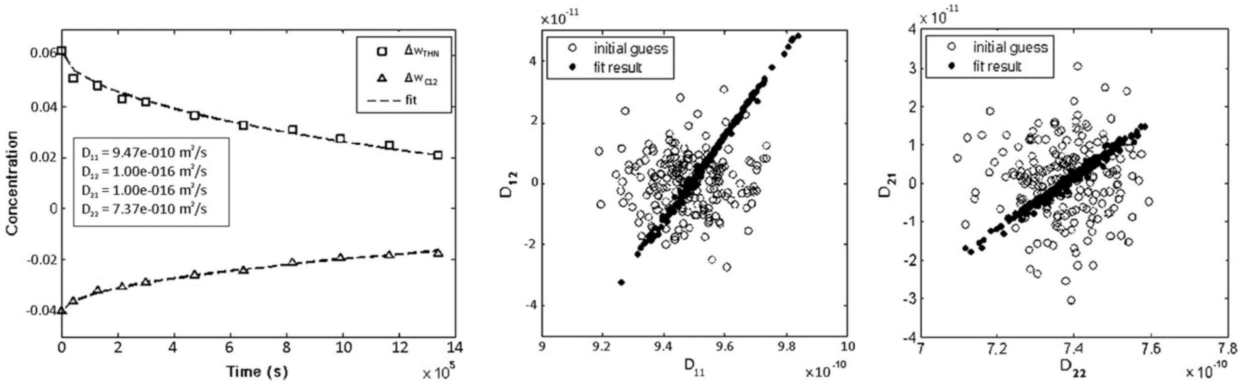


Fig. 6. Results after the second fitting on the calculated points.



(a) (b) (c)

Fig. 7. Results of different fitting procedures: (a) fitting of the experimental points by two-parameter simplex method; (b) and (c) show the dependence of the final fitting results on initial guesses for four-parameter fit by trust region method. Open circles indicate initial guess for pairs of diffusion coefficients (b) D_{12}–D_{11} and (c) D_{21}–D_{22}, while filled circles summarize points to which fitting converges.

and D_{12} are too large in comparison with the largest diffusion coefficients in corresponding binary mixtures [12,14,22]. Therefore, the obtained values for the diffusion coefficients D_{ij} shown in Table 3 cannot be taken as valid, and this requires further investigation.

3.2.2. Fitting tests by simplex and trust region methods using concentration difference

Hereafter the values to be fitted were concentration differences between the upper and bottom parts for components 1 and 2, namely $w_1^{\mathrm{bot}}|_{\mathrm{m}}(t) - w_l^{\mathrm{up}}|_{\mathrm{m}}(t)$ and $w_2^{\mathrm{bot}}|_{\mathrm{m}}(t) - w_2^{\mathrm{up}}|_{\mathrm{m}}(t)$. Two very different fitting algorithms have been used. First is unconstrained Nelder–Mead (*simplex*) method [22] implemented in "*fminsearch*" function of MATLAB. Second is *trust region method*, both unconstrained and constrained, implemented in "*lsqnonlin*" function of MATLAB. Both methods display some advantages and disadvantages, which are discussed in details below.

As the extraction of ternary diffusion coefficients is a very complex task, it is common to divide it on several simple and clear steps. For example, initial step often consists in searching for only diagonal elements of diffusion matrix, assuming cross-diagonal elements vanished. To follow the same approach, D_{12} and D_{21} were fixed to be equal 10^{-16} m^2/s and only D_{11} and D_{22} were varying. In this case, most robust and fast was optimization by simplex method, it converged to the same values of diagonal elements independently of initial guess. Obtained values are reasonable, $D_{11} = 9.47 \times 10^{-10}$ m^2/s and $D_{22} = 7.37 \times 10^{-10}$ m^2/s, see the third line in Table 3. Fitting curves corresponding to these parameters are shown in Fig. 7(a).

But in the next step, when the above diagonal elements were provided as initial guess for four-parameter fit, the *simplex* method fails. In this step the absence of constraints plays a negative role, allowing the *simplex* algorithm to converge to unreasonable values. The *trust region method* appears to be more robust in the case of larger number of fit parameters and better initial guess. To test robustness of the fit, a set of initial guesses generated around 'basic' initial guess with random normal distribution has been used.

Results of the fitting run alone with initial guesses are plotted in parameter space D_{12}–D_{11} and D_{21}–D_{22} in Figs. 7(b, c). Remarkably, fit result forms strait lines in both spaces. Appearance of these lines does not come into surprise as coefficients in both couples 'balance' each other, see Eq. (6). But presence of these lines provides clear insight into problem of appearing and location of unreasonable solutions: all of them seem to converge to the same lines as well, but much far from realistic value.

Among all fit results obtained in the last step one with least magnitude of objective function has been chosen as a provisional result, which is $D_{11} = 9.82 \times 10^{-10}$ m^2/s, $D_{12} = 0.47 \times 10^{-10}$ m^2/s, $D_{21} \sim 0$ m^2/s and $D_{22} = 7.4 \times 10^{-10}$ m^2/s, see the fourth line in Table 3. By the order of the magnitude these values are comparable with diffusion coefficients in corresponding binary mixtures. But strictly speaking these meaningful coefficients cannot be considered as final true value. This conclusion rises from the fact that the trust region method, provided with 'good' initial guess in the vicinity of local minimum of objective function, is unable to find better solution far in parameter space. At the same time, the method fails to converge in case when initial guess is rather far from being good. The results of all the fittings are summarized in Table 3.

Although the results are not reliable, they have been compared to the available results in the literature; for the symmetric point (1:1:1) exists the only one result [23], which was obtained by the Optical Beam Deflection technique in the system with different order of the components (*n*C12–IBB–THN). However, the eigenvalues of diffusion matrix λ_1 and λ_2, Eqs. (4) and (5), do not depend on the order of the components as it is specified in [23].

The comparison of the eigenvalues between our results and those of Ref. [23] (see Table 3) shows a reasonable agreement: λ_1 differs by 8% and λ_2 by 10.5%.

4. Conclusions

An experimental methodology has been developed to determine the variation of the concentration of each component with time. The analytical solution of equations for ternary mixture with boundary conditions corresponding to SST technique has been obtained. Resulting system of two equations contains four unknown diffusion coefficients, D_{ij}. However, four-parameter fitting using "simplex" method and taking into account the restrictions for molecular diffusion coefficients is not enough precise to determine the molecular diffusion coefficients, especially the ones of lower order.

With successfully chosen initial guess the fit by the "trust region method" converges to definite value within close region around this guess; but there is no guarantee that the initial guess is best possible. So, there is some uncertainty still.

Definitely, larger number of experiments would improve the fitting, but it is difficult to define a priori how many experiments are required. This issue can be clarified in the future additional tests.

Another conclusion from the comparison of the results is that researchers should agree on the order of components in ternary mixtures. In recent paper [24] was suggested to choose the denser component as the first one, and then by decreasing of density.

Acknowledgements

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