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Development and validation of a new setup for measurements of diffusion coefficients in ternary mixtures using the Taylor dispersion technique

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ABSTRACT

This paper summarizes our efforts to design and develop a new instrument for measuring the diffusion coefficients in binary and ternary mixtures based on Taylor dispersion technique. The main task was to build a relatively simple instrument with reasonable accuracy which can be applied to a wide range of systems. Previous studies of the diffusion in ternary liquid mixtures were focused at electrolytes and diluted solutions. The mathematical approach was also developed for such kind of systems. We adapted the existing approach for non-dilute mixtures using mass fractions instead of molar concentrations. The experimental protocol and algorithm for the diffusion coefficients extraction were validated against the literature data for the binary system water/isopropanol. We report the results of the measurements of diffusion coefficients in symmetric point (1:1:1) of ternary mixture THN/IBB/C12.

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1. Introduction

Knowledge of mass diffusion coefficients has a great importance in many fields of applied sciences. Our particular interest for measuring isothermal diffusion is linked with investigations into the Soret effect. The mass transport in multicomponent systems is more complicated in comparison with binary mixtures due to a complex interplay between heat and mass transfer processes. Presently there exist well-established methods for measurement of thermodiffusion coefficients in binary mixtures [1–4]. Some of them measure thermodiffusion coefficients D_T while others the Soret coefficient, S_T. For binary mixtures, the relation between these two coefficients is simple: $S_T = D_T/D$, and, consequently, thermodiffusion and Soret coefficients have the same sign.

In ternary (and higher) mixtures, the cross-molecular diffusion complicates measurement of these coefficients in comparison to binary mixtures. The diffusive mass transport of a given component is induced not only by its compositional gradient (main or principal diffusion), but also by the compositional gradients of the other components (cross-diffusion) and the temperature gradient. If we denote the mass fraction of component i by C_i, then the diffusive flux of this component can be written as:

$$J_i = -\rho \sum_{k=1}^{N-1} D_{ik} \nabla C_k - \rho D'_{Ti} \nabla T, \quad i = 1, 2, 3, \ldots, N \tag{1}$$

where D_{ik} are the mass-based diffusion coefficients and D'_{Ti} are the thermal diffusion coefficients.

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The Soret coefficients in the ternary mixture ($N = 3$) can be determined as [5,6]:

$$S_{T1} = \frac{D_{T1}D_{22} - D_{T2}D_{12}}{D_{11}D_{22} - D_{12}D_{21}}, \qquad S_{T2} = \frac{D_{T2}D_{11} - D_{T1}D_{21}}{D_{11}D_{22} - D_{12}D_{21}} \tag{2}$$

It follows from Eq. (2) that the signs of the Soret coefficients not only depend on D_{Ti}, but also can be affected by the main diffusion and cross-diffusion coefficients. The best way to have the necessary data concerning mass diffusion coefficients is to measure them by an independent technique, with a reasonable accuracy, which can be applied to a wide range of systems.

This paper aims to report the development and validation of an instrument for measuring mass diffusion coefficients in the ternary mixtures which are of interest in the DCMIX project of the European Space Agency.

2. Experimental procedure and equipment

The usual procedure of Taylor dispersion technique [7] is to inject a sample solution into the laminar flow of the liquid flowing in a long capillary tube. This injected sample must have a small volume and a slightly different concentration than the investigated "carrier" solution. Unlike to the chromatographic studies, it is the carrier liquid which is under investigation. At a constant temperature, the liquid carrier flows with constant velocity through a capillary with an inner radius r. At the end of the capillary, a detector monitors and records the change in concentration. Due to Poiseuille parabolic velocity profile:

$$U(r) = 2u\left[1 - \left(\frac{r}{R}\right)^2\right] \tag{3}$$

a radial diffusion flux appears and the injected "square" pulse develops into a Gaussian concentration profile. Here u is the mean velocity of the carrier flow, R is the radius of the capillary, and r is the radial coordinate, measured perpendicularly to the axis of the tube.

The following substances from Acros Organics were used: water pure, deionized reagent Grade 3 (CAS Number: 7732-18-5); isopropanol for HPLC gradient grade, 99.5% (CAS Number: 67-63-0); tetralin (1, 2, 3, 4-tetrahydronaphthalene), 98% (CAS Number: 119-64-2); isobutylbenzene, 99.5% (CAS Number: 538-93-2); n-dodecane, 99% (CAS Number: 112-40-3).

The setup used in the experiments is shown schematically in Fig. 1. The pump has to produce a constant and laminar flow. We chose the Knauer S1000 HPLC (High-Pressure Liquid Chromatography) analytical pump with active pulsation dampening. To prevent bubbles from disturbing the flow, the SYSTEC degassing module is installed and connected in-line before the pump. The flow rate during the measurements was 0.079 ml/min. Zero dead volume fittings are used to connect the dispersion tube with the six port injection valve (sample loop volume 20 μL). The utilized Knauer Smartline RI Detector 2300 is suited for recording small concentration variations by its differential sensitive refractometer.

Typical value of the base line noise was not more than $\pm 1.5 \times 10^{-8}$ refractive index unit (RIU). Digital data acquisition and control of the auto-zero feature, as well as rinsing functions, were carried out from a computer interacting with the pump and the detector. The Teflon dispersion tube has a length of 29.839 ± 0.001 m and an effective radius of 374 μm. The capillary is coiled on a grooved aluminum cylinder in the form of a helix of diameter 30 cm. The RI detector and the dispersion tube are kept at constant temperature of 298.15 ± 0.1 K using a temperature-regulated air bath. The mixtures were prepared by weighing each component using electronic balances manufactured by Sartorius with resolution 0.1 mg/160 g or 0.01 g/4000 g. The possible error in mass fraction is estimated to be around 0.00001.

3. Mathematical approach

3.1. Binary diffusion

To measure the diffusion coefficient D in binary mixtures, samples of mixtures containing the component at mass fraction $C_0 + \Delta C$ were injected into the laminar carrier solution of composition C_0. At time t after an injection, the concentration profile of the dispersed sample flowing through the tube can be derived analytically, see [8–10]:

$$C(t) = C_0 + \frac{2\Delta C \Delta Vol}{R^3 u}\sqrt{\frac{3D}{\pi^3 t}}\exp\left(-\frac{12D(t - t_R)^2}{R^2 t}\right) \tag{4}$$

where $t_R = L/u$ is the retention time; L is the length of the dispersion tube, and ΔVol is the volume of the injected solution sample. Eq. (4) is the analytical solution of the differential equation for the case of radial diffusion inside a tube of circular cross section.

Considering the signal of the refractive index detector instead of concentration, Eq. (4) can be written as:

$$V(t) = V_\infty + V_1 t + \Delta V_{max}\sqrt{\frac{t_R}{t}}\exp\left(-\frac{12D(t - t_R)^2}{R^2 t}\right) \tag{5}$$

where ΔV_{max} is the peak height relative to the base line; the two terms $V_\infty + V_1 t$ allow us to take into account a drift of the base line.
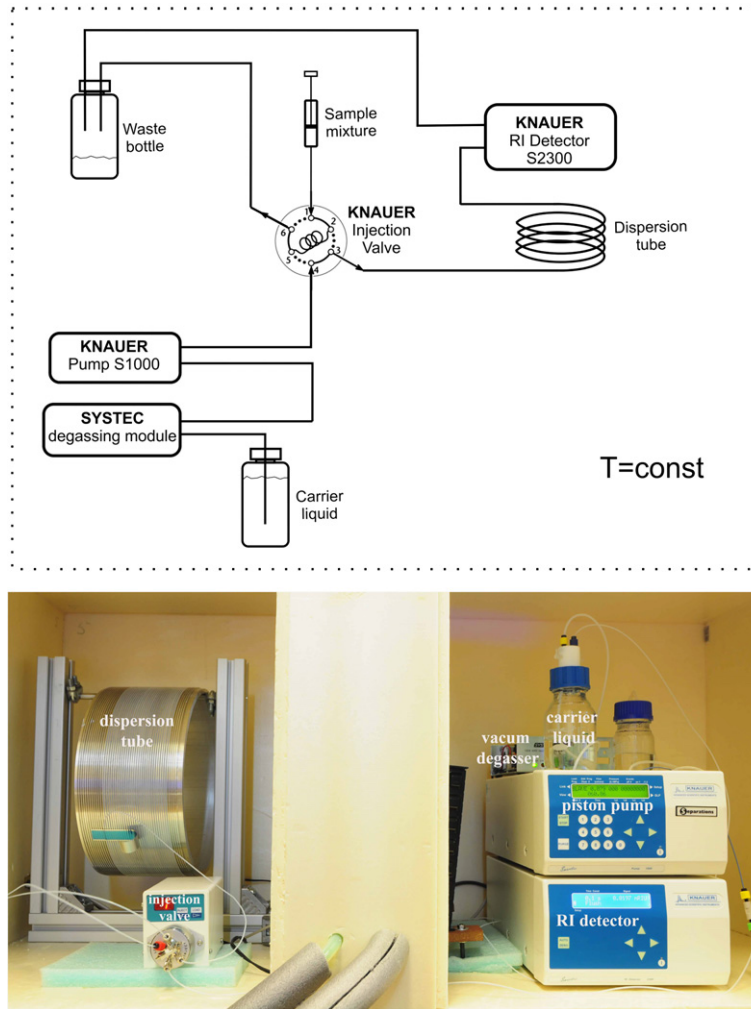
Fig. 1. Principle scheme of the experimental setup and its photo.

Concentration differences ΔC must be sufficiently small to ensure that the changes in the detector signal $V(t)$ would be proportional to the changes in solute concentration across the dispersion profiles:

$$V(t) - V_\infty = S[C(t) - C_0] \tag{6}$$

where $S = \partial V / \partial C$ is the detector's sensitivity.

3.2. Ternary dispersion profiles

Ternary dispersion profiles are generated by a similar procedure, injecting small samples of mixtures containing components 1 and 2 with mass fractions $C_1 + \Delta C_1$ and $C_2 + \Delta C_2$ into the carrier stream, of composition C_1 and C_2. All the equations describing ternary profiles contain eigenvalues of the diffusion coefficients matrix D_{ik}:

$$D^{(1)} = \frac{D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}}{2} \tag{7}$$

$$D^{(2)} = \frac{D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}}{2} \tag{8}$$

For ternary mixtures, time dependencies of radially averaged concentrations of the dispersed components at the outlet of the tube were obtained in the following form [11]:

$$C_1(t) = C_1 + \frac{2\Delta Vol}{R^3 u}\sqrt{\frac{3}{\pi^3 t}}\left(A_{11}\sqrt{D^{(1)}}\exp\left(-D^{(1)}\eta\right) + A_{12}\sqrt{D^{(2)}}\exp\left(-D^{(2)}\eta\right)\right) \tag{9}$$

$$C_2(t) = C_2 + \frac{2\Delta Vol}{R^3 u}\sqrt{\frac{3}{\pi^3 t}}\left(A_{21}\sqrt{D^{(1)}}\exp\left(-D^{(1)}\eta\right) + A_{22}\sqrt{D^{(2)}}\exp\left(-D^{(2)}\eta\right)\right) \tag{10}$$

where η is an abbreviation for $12(t - t_R)^2/R^2 t$; A_{ik} coefficients are defined as follows:

$$A_{11} = \frac{\frac{(D_{22}-D^{(1)})\Delta C_1}{M_1} - \frac{D_{12}\Delta C_2}{M_2}}{D^{(2)} - D^{(1)}} \tag{11}$$

$$A_{12} = \frac{\frac{(D_{22}-D^{(2)})\Delta C_1}{M_1} - \frac{D_{12}\Delta C_2}{M_2}}{D^{(1)} - D^{(2)}} \tag{12}$$

$$A_{21} = \frac{\frac{(D_{11}-D^{(1)})\Delta C_2}{M_2} - \frac{D_{21}\Delta C_1}{M_1}}{D^{(2)} - D^{(1)}} \tag{13}$$

$$A_{22} = \frac{\frac{(D_{11}-D^{(2)})\Delta C_2}{M_2} - \frac{D_{21}\Delta C_1}{M_1}}{D^{(1)} - D^{(2)}} \tag{14}$$

where M_1 and M_2 are molecular weight for components 1 and 2 correspondingly.

3.3. Basic equations for ternary mixtures and fitting procedure

The working equations for ternary mixture are different for the case of distinct or equal eigenvalues. Hereafter we consider the case of distinct eigenvalues. The detector's signals for ternary diffusion resemble two superimposed Gaussian curves centered on time t_R with variances $R^2 t_R/(24 D^{(1)})$ and $R^2 t_R/(24 D^{(2)})$. Using $S_1 = (\partial V/\partial C_1)_{C_2}$ and $S_2 = (\partial V/\partial C_2)_{C_1}$ to denote the RI detector sensitivities with respect to components 1 and 2 in the mixture, the equation for the signal can be derived as:

$$V(t) = V_\infty + V_1 t + S_1\left[C_1(t) - C_1\right] + S_2\left[C_2(t) - C_2\right] \tag{15}$$

Substituting Eqs. (9) and (10) into Eq. (15), including the linear baseline term, gives a basic equation for the detector's signal:

$$V(t) = V_\infty + V_1 t + \Delta V_{max}\sqrt{\frac{t_R}{t}}\left(W_1\exp\left(-D^{(1)}\eta\right) + (1 - W_1)\exp\left(-D^{(2)}\eta\right)\right) \tag{16}$$

where W_1 is a normalized weight.

The eigenvalues and A_{ik} coefficients in Eqs. (11)–(14) are functions of the diffusion coefficients D_{ik}.

To simplify the analysis of ternary diffusion profiles, it is useful to introduce parameters a and b following papers by D.G. Leaist and co-authors [12,13] and perform four parameter fittings in space $D^{(1)} - D^{(2)} - a - b$:

$$a = \frac{(D_{11} - D^{(1)} - \frac{S_1 D_{12}}{S_2})}{D^{(2)} - D^{(1)}}, \qquad b = \frac{(D_{22} - D_{11} - \frac{S_2 D_{21}}{S_1} + \frac{S_1 D_{12}}{S_2})}{D^{(2)} - D^{(1)}} \tag{17}$$

In this case, the equation for normalized weight W_1 in Eq. (16) can be written as:

$$W_1 = \frac{(a + b\alpha_1)\sqrt{D^{(1)}}}{(a + b\alpha_1)\sqrt{D^{(1)}} + (1 - a - b\alpha_1)\sqrt{D^{(2)}}} \tag{18}$$

where α_1 is fraction of the refractive index variation induced by variation of the concentration of component 1:

$$\alpha_1 = \frac{1}{1 + \frac{S_2 M_1 \Delta C_2}{S_1 M_2 \Delta C_1}} \tag{19}$$

If the diffusion matrix is well conditioned, the eigenvalues $D^{(1)}$ and $D^{(2)}$ as well as a and b can be reliably evaluated by using nonlinear least-squares technique to fit Eq. (5) for two and more dispersion profiles. For example, it may be two profiles with values of α_1 such as $\alpha_1 = 0$ ($\Delta C_1 = 0$) and $\alpha_1 = 1$ ($\Delta C_2 = 0$), and one profile with value of α_1 between 0 and 1. The ratio of detector sensitivities S_1/S_2 between components 1 and 2 in the mixture can be evaluated by taking the ratio of peak areas of profiles with respect to the base line:

$$\frac{S_1}{S_2} = \frac{Surf_1 \Delta C_2}{Surf_2 \Delta C_1} \tag{20}$$

Table 1
Measured diffusion coefficients ($D/10^{-10}$, $m^2 s^{-1}$) for the binary mixtures of water and isopropanol.

C_{water}	0.1	0.7	0.792	0.901
Injection 1	5.02	2.40	4.29	7.04
Injection 2	5.06	2.44	4.31	6.98

where $Surf_1$ and $Surf_2$ are the surface areas between the dispersion profiles and the base line generated for the case when $\alpha_1 = 0$ and 1.

Then, the equation for normalized weight W_1 will have the following form [12,13]:

$$D_{11} = D^{(1)} + \frac{a(1-a-b)(D^{(1)} - D^{(2)})}{b} \tag{21}$$

$$D_{12} = \frac{S_2 a(1-a)(D^{(1)} - D^{(2)})}{S_1 b} \tag{22}$$

$$D_{21} = \frac{S_1(a+b)(1-a-b)(D^{(2)} - D^{(1)})}{S_2 b} \tag{23}$$

$$D_{22} = D^{(2)} + \frac{a(1-a-b)(D^{(2)} - D^{(1)})}{b} \tag{24}$$

4. Results

For the extraction of the mass diffusion coefficients from binary and ternary dispersion profiles, we developed a MATLAB program based on the constrained active-set quadratic programming algorithm described in [14,15]. Realization of this mathematical algorithm consists of two steps. The first step involves the rough evaluations of the space parameters D_{ik} (when possible). An iterative sequence of runs that converge to the solution is generated at the second step inside the parameter space determined at the first step. The criteria of the optimization procedure corresponded to the minimum of the residual function, which was estimated like a sum of the squared differences between experimental and calculated signals.

In the preliminary step of the fitting procedure, the base line parameters V_∞ and V_1 as well as the retention time t_R and peak height ΔV_{max} were estimated from experimental signals. During processing of the ternary dispersion profiles, the ratio between detector sensitivities $S_1 = (\partial V/\partial C_1)_{C_2}$ and $S_2 = (\partial V/\partial C_2)_{C_1}$ was determined by taking the ratio of the peak areas generated by some excess amount of components 1 and 2 into the carrier solution. During the second step, dispersion profiles were analyzed by fitting Eq. (16) to the measured signals treating a, b, $D^{(1)}$ and $D^{(2)}$ as adjustable parameters. In case of binary mixtures, only diffusion coefficients were taken as adjustable parameters in Eq. (5).

The performances of the new setup and algorithm of the diffusion coefficients extraction were tested for binary mixtures of water and isopropanol. This mixture was comprehensively studied [2] using different techniques: thermogravitational column (TGC) in combination with sliding symmetric tubes (SST), optical beam deflection (OBD), optical digital interferometry (ODI), and microgravity measurements (SODI/IVIDIL) on the International Space Station (ISS). The agreement between values from Table 1 and diffusion coefficients measured by other techniques is more than satisfactory (see Fig. 2). Within the experimental precision the different injections gave identical results (see Table 1).

In the case of ternary mixtures, the developed experimental protocol and the fitting program were firstly applied for measurements of diffusion coefficients at the symmetric point (1:1:1 in mass fraction) of the mixture tetralin (THN), isobutylbenzene (IBB) and n-dodecane (nC12). The two samples with compositions close to the symmetric point were prepared to be injected into the carrier liquid. The compositions of the samples and parameters of the experiment are listed in Table 2. The experiment was repeated two times with each injection sample. Fitting was conducted using simultaneously the signals of four injections.

Fitting has been performed under the following constraints for the diffusion matrix D_{ik}:

$$D_{11} > 0, \qquad D_{22} > 0$$

$$D_{11}D_{22} - D_{12}D_{21} > 0 \tag{25}$$

$$(D_{11} - D_{22})^2 + 4D_{12} \cdot D_{21} \geqslant 0 \tag{26}$$

Experimental signals and fitting curves are shown in Fig. 3 and they demonstrate excellent quality of fit. During the fitting procedure, standard deviation for the residual function did not exceed 1×10^{-8}. Presently, there many attempts to measure diffusion coefficients at the symmetric point of THN/IBB/nC12 as the thermodiffusion coefficients were measured only at this point [16,17]. Results for diffusion coefficients measured by SST (sliding side technique) [18] may be found in this issue of the journal.
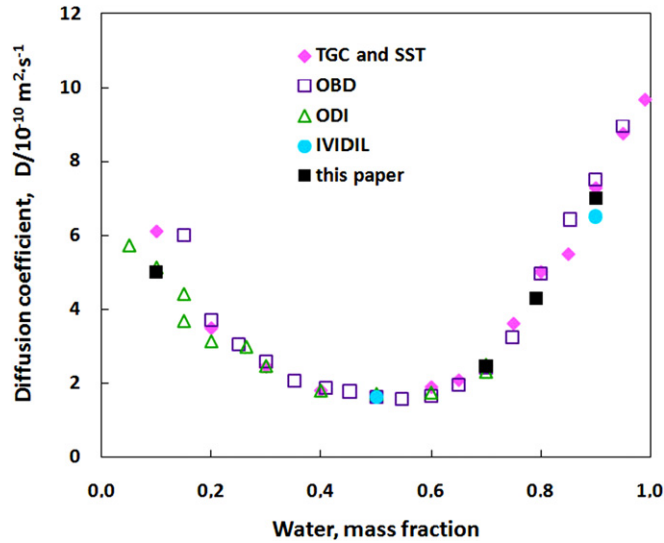
Fig. 2. Diffusion coefficients for the binary system water/isopropanol obtained by different measurement techniques.

Table 2
Concentration of components (mass fraction) in mixture THN/IBB/nC12 and experimental parameters.

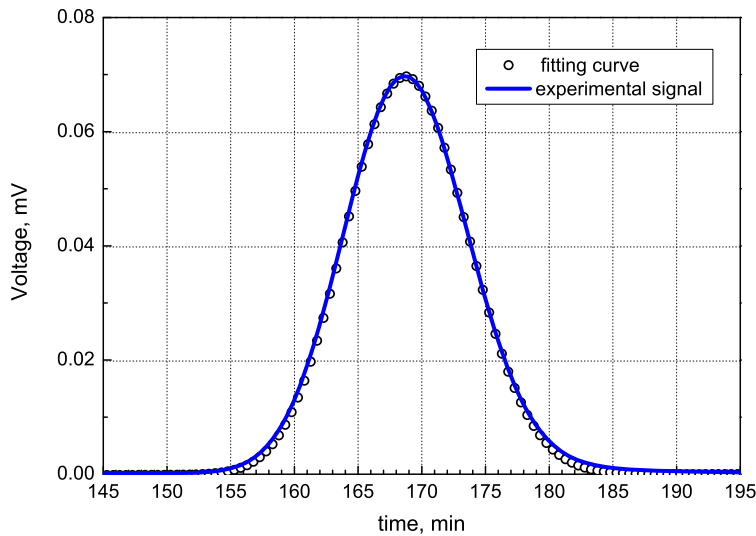| Carrier mixture C_{THN}/C_{IBB}	Injection sample 1 C_{THN}/C_{IBB}	Injected sample 2 C_{THN}/C_{IBB}	Retention time t_R	$Surf_1$	$Surf_2$	S_1/S_2
0.33336/0.33336	0.30040/0.33278	0.33305/0.299943	10 112 s	86.5	52.4	1.65

Fig. 3. Ternary dispersion profile and fitting curve obtained in ternary mixture THN/IBB/nC12 with composition 1:1:1 (mass fraction) at 298.15 K.

Comparison of diffusion coefficients presented in Table 3 indicates that the novel instrument for the Taylor dispersion technique is working properly and that the computer program for fitting is working satisfactory.

5. Conclusions

The novel instrument for accurate measurements of mass diffusion coefficients by the Taylor dispersion technique was successfully developed. The instrument is validated by measuring diffusion in binary mixture water/isopropanol and comparing with literature data. The diffusion coefficients was measured in the ternary mixture THN/IBB/nC12 at the point with equal mass fractions. Comparison with the available data for this ternary mixture obtained by different experimental methods have shown favorable agreement.

Table 3

Diffusion coefficients measured in mixture THN/IBB/nC12 with composition 1:1:1 (mass fraction) at 298.15 K.

D/10^{-10}, m^2 s^{-1}	This paper	Sliding symmetric tubes [18]
D_{11}	8.93 ± 0.1	9.35
D_{12}	1.61 ± 0.05	0.047
D_{21}	-1.44 ± 0.04	0
D_{22}	5.83 ± 0.015	7.87
$D^{(1)}$	7.67	9.35
$D^{(2)}$	7.09	7.87

Acknowledgements

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