Evaluation of Diffusion Coefficient Determination using a Microfluidic Device

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A theoretical description of the convection-diffusion process in a homogeneous system enabling estimation of diffusion coefficients employing commercially available Y-junction microchannel is presented. A detailed numerical analysis based on finite volumes and finite differences, namely the explicit, implicit and Crank-Nicolson method, was performed and analyzed on the same domain in order to verify the proposed models. All numerical approaches provided stable solutions with certain numerical variations depending on the number of iterations defined by the mesh density. In addition, the method was validated with measurements of diffusion coefficients of some selected components in the short Y-junction microchannel. Benefits and possible pitfalls of this estimation method are discussed.

Key words:
diffusion coefficient, microfluidic device, Y-junction microchannel, mathematical model, numerical methods

Introduction

Diffusion is an important transport phenomenon that plays a major role in many applications. This holds true for microreactor technology, where diminished diffusion times related to small channel dimensions often lead to process intensification.[1] While laminar flow indicated by the low Reynolds numbers provides a carefully controlled environment where convective mass transfer occurs in the direction of the fluid flow, mixing in microchannels can be achieved solely by molecular diffusion.[2] Quantitative analysis of diffusion is therefore a necessity for the efficient design and optimization of nearly all processes in microfluidic devices, while accurate determination of diffusion coefficients represents a very important step in understanding and modeling transport phenomena that take place in the chosen system. This includes modeling of the kinetics of phase transitions, extractions, chemical reactions, dialysis, and biochemical assays, among others.[3,4]

Owing to the considerable effort needed to measure liquid phase diffusion coefficients, empirical correlation equations are preferably used for their estimation. Most of them include empirical constants that are based on experimental data; they require knowledge of solutes' and solvents' properties and are usually proposed for specified conditions and systems. The accuracy of diffusion coefficients estimated by the correlations is therefore questionable and can sometimes have a significant effect on the interpretation of experimental results. Values estimated by correlations generally agree with experimental values within 5 to 10 %, although discrepancies of more than 20 % are possible.[5] Considering these limitations, in addition with incomplete database on species properties, especially in the case of arbitrary conditions, further studies employing efficient method of measurement are needed in order to obtain solute diffusion coefficient values in any given liquid system.

Techniques for diffusion coefficient estimation based on monitoring macroscopic concentration gradients include the diaphragm cell,[3] pulsed gradient NMR,[6] light scaterring[4] and Taylor tube dispersion.[7] In the last decade, microfluidic devices and lab-on-a-chip technology have exerted a substantial impact on chemical analysis, biomedical applications, and chemical synthesis, along with others.[8] Their microscale dimensions make diffusion a rapid separation mechanism for extraction of small molecules from the stream of the fluid. Determination of diffusion coefficient in microfluidic devices requires very small sample volumes (under 1 mL) and amounts of diffusing species (25–500 pmol) and could therefore be preferable to the conventional analytical techniques, which are usually complex, time consuming and tedious.[9,10] Also the time needed to obtain the results with micro devices is shorter, only a few minutes or even seconds.[10] For measurements of diffusion coefficient in continuously operated microfluidic devices, the so called T-sensor and H-cell have received significant attention in recent years.[11,12] Diffusion coefficients within T-sensor were already successfully measured for small molecules and proteins ranging in mass from

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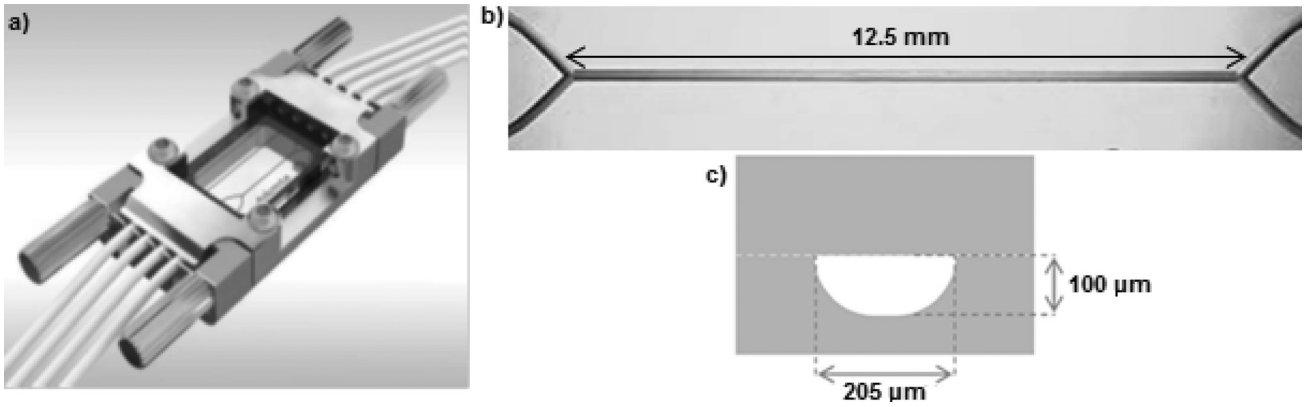

Fig. 1 – *Microfluidic device used for measurement of diffusion coefficient: a) microfluidic chip inserted into chip holder with inlet and outlet PEEK tubes;[17] b) Y-junction microchannel; c) cross-section of the microchannel[17]*

800 Da to 66 kDa.[10,13] Culbertson *et al*.[14] compared four methods employing the effects of the electric field within a microfluidic device, a static imaging method in the absence of electric field (i.e. with no fluid flow) and three dynamic methods, where the analyte was moving under the influence of an applied electric field. Dynamic measurements of the diffusion coefficient of rhodamine 6G were 11 % larger than measured by a static method. All four methods were based on fluorescence detection, where UV light excitation for fluorescent dye was used for observing the fluid in a microfluidic device. Since fluorescence microscopy requires the addition of dyes, which can affect the samples, especially in the case of biological applications and can be applied only to selected materials, dye-free techniques to visualize the analyte distribution inside microchannels like LAPS (light-addressable potentiometric sensor),[15] Brownian microscopy[16] and confocal Raman microscopy[8] are also used.

The aim of this work was to define and identify the theoretical basis, experimental design, and computational methods, all necessary to use a microfluidic device as a tool for accurate determination of diffusion coefficients in homogeneous systems. A detailed numerical analysis was performed to verify the proposed models. In addition, the method was validated with measurements of diffusion coefficients of some selected components in the short Y-junction microchannel.

Experimental

Materials

Chemicals

Methylene blue, acetophenone and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). Diffusion coefficient of acetophenone was measured in 20 mM sodium phosphate buffer (pH 7) prepared from disodium hydrogen phosphate dihydrate from Sigma-Aldrich (Steinheim, Germany) and sodium dihydrogen phosphate monohydrate from Merck (Darmstadt, Germany). In case of aqueous solutions purified water was used.

Microfluidic devices and experimental set-up

Fluid flow analysis was made in a glass microchip with Y-shaped inlet and outlet junctions (Micronit Microfluidics B.V., Enschede, The Netherlands). Dimensions of the custom-made microchannel were 50 µm, 220 µm and 33.2 cm regarding depth (d), width (w), and length (l), respectively. For diffusion coefficient determination, a commercially available glass Y-junction chip was used (Dolomite Ltd., Royston, UK). Microchannel dimensions ($d \times w \times l$) were 100 µm x 205 µm x 12.5 mm. The chip was designed to fit inside a stainless steel housing (Dolomite Ltd., Royston, UK) and was, just like the chip for the flow analysis, connected with polyether ether ketone (PEEK) tubes (VICI Jour, Schenkon, Switzerland) to high performance syringe pumps (PHD 4400 Syringe Pump Series, Harvard Apparatus, Holliston, MA, USA) equipped with steel syringes (8 mL). The syringe pumps ensured precisely controlled, adjustable flow rates.

Methods

Determination of viscosities and densities

Viscosities of solutions were determined with Cannon-Fenske viscometer (The Emil Greiner Co., New York, USA), which was thermostated at 23 °C, while densities were measured using a 10 mL pycnometer (Carl Stuart Ltd., Leek, UK).

Fluid flow analysis

The fluid flow inside the microfluidic device was observed during an experiment where methylene blue dissolved in water was fed from one in-

flow and pure water from the other. Using syringes and syringe pumps, the flow was precisely controlled and flow rates of both inflows were set equal. After achieving steady state conditions, fluid within a microchannel was observed with optical microscope (Reichert 310, Depew, NY, USA), while photos were taken with Aigo GE-5 digital microscope (Beijing Huaqi Information Digital Technology Co., Ltd., Beijing, China).

Determination of diffusion coefficients within a microchannel system

Y-junction chip was used for diffusion coefficient estimation of selected solute in selected solvent. Chip was connected to two syringe pumps where one syringe was filled with solute dissolved in solvent, while other was filled with solvent only. When both solutions were fed to the microchannel through separate inlets, flow rate values on both pumps were set equal. The experiments were performed at ambient temperature (23 °C) and steady state conditions at total flow rates from 40 to 70 μL min^{-1}, which ensured residence times that were long enough for accurate detection of solutes at both exits.

Analysis of solute concentrations

Samples for analysis were taken at the inlet and from both outlets of the channel and solute concentrations were determined with spectrophotometric absorption measurements. At least three parallels were analyzed and the mean values were calculated. Maximum deviation of experimental measurements from the mean values was less than 1 %. Analysis was performed off-line using a spectrophotometer Cary 50 UV/Vis (Varian Australia Pty Ltd., Mulgrave, Australia). Prior to spectrophotometric measurements, samples were diluted as needed. Concentrations of methylene blue and acetophenone in selected solvents were determined by measuring absorption at 600 and 245 nm, respectively.

Prediction of diffusion coefficients

Since Stokes-Einstein equation specifically applies to a solute whose molecular diameter is large compared to that of the solvents and which has roughly spherical shape, it has been successfully used as a starting point for many correlation equations for estimating liquid phase diffusion coefficients.[18]

Wilke-Chang correlation[18] is an empirical modification of the Stokes-Einstein equation and is probably the most widely used one. It is successfully employed for dilute, binary mixtures of low molecular weight non-electrolytes in liquids. The correlation in Eq. (1) applies for very dilute solutions and gives an estimated error of 20 %[19]:

$$D_{AB} = \frac{7.4 \cdot 10^{-8} \left(\Phi_B M_B\right)^{0.5} T}{\mu_B V_A^{\,0.6}} \tag{1}$$

where D (cm^2 s^{-1}) presents diffusion coefficient, while A and B denote solute and solvent, respectively. Φ_B is the association factor of the solvent (dimensionless) and M_B is molecular weight of the solvent (g mol^{-1}), T is temperature (K), μ_B is solvent viscosity (mPa s) and V_A is molar volume (mL mol^{-1}) of liquid solute at its normal boiling point. Wilke and Chang[18] recommended that Φ_B should be chosen as 2.6 if the solvent is water, 1.9 if it is methanol, 1.5 if it is ethanol and 1.0 if it is unassociated.

Scheibel correlation (Eq. (2)) is a modified Wilke-Chang correlation with eliminated association factor and is used for smaller molecules of the solute.[18,20]

$$D_{AB} = \frac{8.2 \cdot 10^{-8} T}{\mu_B V_A^{1/3}} \left[1 + \left(\frac{3V_B}{V_A}\right)^{2/3}\right] \tag{2}$$

where V_B is molar volume (mL mol^{-1}) of a solvent at its normal boiling point, while the other symbols used are the same as in Eq. 1.

Both Wilke-Chang and Scheibel correlation can be used for estimating diffusion coefficients in aqueous organic mixtures (i.e. methanol/water or acetonitrile/water systems) and Li and Carr[20] found that the Scheibel equation is the more accurate. In case of solvent mixtures, the molecular weight, association factor and molar volume of the mixture need to be calculated.

For aqueous solutions, an alternative model used is the Siddiqi-Lucas correlation (Eq. (3)) and presents an estimated error of 13 %.[19]

$$D_{AB} = 2.98 \cdot 10^{-7} \frac{T}{V_A^{0.5473} \mu_B^{1.026}} \tag{3}$$

where all the symbols used are the same as in Eq. 1.

Properties of the solutes and solvents that were used for calculating diffusion coefficient from selected empirical correlations are gathered in Table 1.

Table 1 – *Properties of selected solutes and solvents*

Solute (A)	Solvent (B)	V_A [mL mol^{-1}]	V_B [mL mol^{-1}]	M_B [g mol^{-1}]	T [K]	μ_B [mPa s]	Φ_B [/]
Methylene blue	Water	260.04	18.069[21]	18.02	296.15	0.889	2.6[18]
Acetophenone	Aqueous phosphate buffer + 10 % Methanol	117.366[21]	20.332[20]	19.42	296.15	0.988	2.5[20]

Model development for determination of diffusion coefficient

Governing equations

A theoretical description of the diffusion of one component in a homogeneous system was developed using the bases of continuum theory.

First, the fluid velocity profile for laminar flow in steady state was calculated with numerical solution to Eqs. 4 and 5:

$$\vec{u} \cdot \nabla \vec{u} - \nu \nabla^2 \vec{u} + \nabla p = 0 \tag{4}$$

$$\nabla \cdot \vec{u} = 0 \tag{5}$$

where $\vec{u}$ is the velocity vector (m s^{-1}), p is the kinematic pressure (m^2 s^{-2}) and ν is the kinematic viscosity (m^2 s^{-1}). At inlets velocity was defined by the set volumetric flow rate, at microchannel walls the so called no-slip boundary where velocity is zero ($\vec{u} = 0$) was used, while at outlets gradient of velocity perpendicular to the surface was zero. The pressure was defined at outlet and zero gradient of pressure perpendicular to the channel wall surface was defined elsewhere.

Concentration profile was therefore calculated separately from the velocity by numerical solution to Eq. 6 in steady state with the defined concentrations at the inlets and zero gradient of concentration perpendicular to the wall surface elsewhere:

$$\vec{u} \cdot \nabla c_A - D_{AB} \nabla^2 c_A = 0 \tag{6}$$

where c_A is the concentration of the solute A, D_{AB} is the diffusion coefficient of the solute A in solvent B and $\vec{u}$ is the velocity vector obtained from Eqs. 4 and 5.

Numerical methods

Finite difference/volume/element methods, which base on the discretization of continuous form of transport equations, are the most common macroscale simulation techniques for the numerical solving of partial differential equations (PDEs). They are all very well-established, computationally efficient, and with the development of powerful CFD software tools, such as COMSOL Multiphysics® (FEM), OpenFOAM® (FVM), MATLAB®, *Mathematica*® (FDM), also available to the wider users unfamiliar with techniques in numerical methods. Of the listed methods the FDM is probably the most simple for understanding and implementation, however, while FEM and FVM can be applied to uniform and non-uniform meshes, FDM is basically solved through a fixed, rectangular geometry. Nevertheless, the uniform grids inherent to FDM make it very intuitive to learn and to program. In our work the finite difference/volume methods were used in numerical analysis.

Results and discussion

Determination of the diffusion coefficient using a microfluidic device requires experimental and numerical skills and experiences. To obtain reliable and repeatable experimental values, which are the basis for further numerical processing and analysis, it is necessary to ensure the stable operational and process conditions. In other words, the experimental setup must provide the transport of measured component from one inflow to the other outflow only by diffusion along the straight or curved microchannel. Therefore, the selection of the appropriate microchannel and its connection with the pumps, which must ensure a continuous flow without any pulsations, is crucial. In the selection of the microchip, the surface roughness of the channel walls is important as well as the shape of the microchannel. Due to different fabrication processes and materials used, microchannel cross-sections are mostly not circular in shape and the evaluation of the flow characteristics with regard to the shape should be considered.[22] Namely, when both inflows at the same flow rate enter the microchannel through a symmetrical Y-shaped or even T-shaped inlet, the flat junction surface in the middle of microchannel is formed at laminar and stationary flow conditions (Fig. 2).

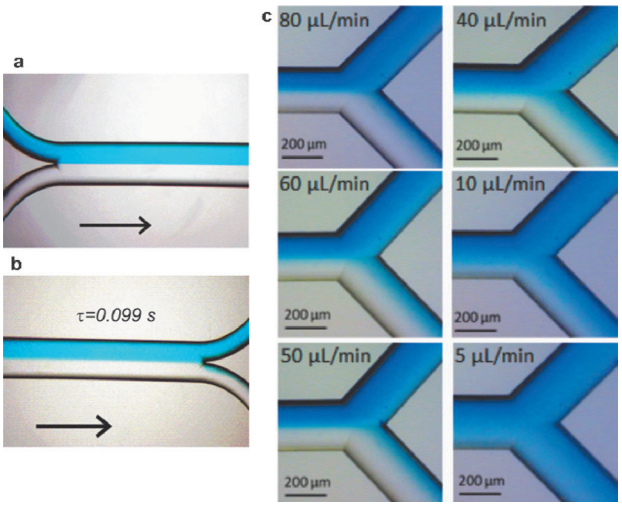

Fig. 2 – *The flat junction surface in the middle of microchannel formed from the inlet (a) to the outlet (b) at the laminar and stationary flow conditions (microchannel with dimensions $w \times d \times l$ = 220 µm × 50 µm × 33.2 cm; flow rate of each inflow is 100 µL min^{-1}); (c) evolution of the diffusion front at the exit of the 12.5 mm long microchannel for diffusion coefficient determination at applied different flow rates of methylene blue solution with initial concentration 3·10^{-3} mol L^{-1} and pure water*

In smooth channels, with the relative roughness around 1 µm, such an interface through which the mass transport of the component takes place only by diffusion, is reestablished along the whole

straight or curved microchannel and should end exactly in the middle between the output of the Y-shaped channel or H-cell. Thus the equality of flow rates of "left" and "right" oriented inflows and outflows is provided. Moreover, the real contact surface area along the channel with dimension of the channel length times depth is then accurately approximated by the flat "diffusion surface" in physical domain. In addition to providing a constant temperature, some details of the experimental setup like the equal length of the connecting tubes between the pumps and the microchannel, as well as the outlet tubes, play an important role in the accuracy of the measurements. Also, the prior filtering of the liquid phase is recommended in order to prevent entry and accumulation of trash at the microchannel outlet (Fig. 3) and therefore the undesirable convectional mixing of two main streams at the microchannel outlet. The selection of a transparent microchannel allows the additional visual control of flow conditions inside the microchannel before and during the measurement.

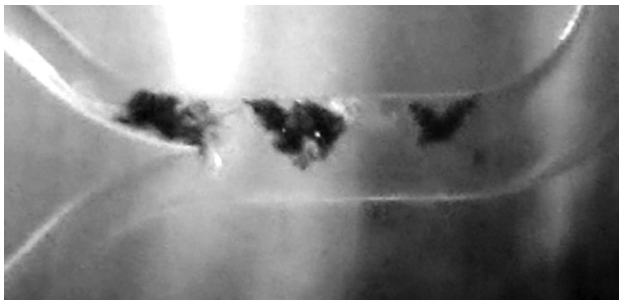

Fig. 3 – *An example of accumulated trash at the Y-shaped outlet of the glass microchannel*

Irrespective of all the above mentioned, a decision with regard to the residence times and related flow rates, cross-section and length of the channel is essential. In general, we need to provide such residence times in the microfluidic device that the quantities of a given component in both outflows are in the range of accurate analysis. In case of diffusion coefficient determination for bigger and therefore slower molecules, longer and probably curved microchannels are favored. Logically, the preliminary numerical simulations give us the best answers regarding the selection of appropriate dimensions of microfluidic device and process conditions. If we want to determine the diffusion coefficient of some biological molecules in unconventional liquid, such as deep eutectic solvent or ionic liquid (IL) with very high viscosity, the diffusion coefficient around 10^{-11} m^2 s^{-1} can be expected. Based on the simulations, it can be demonstrated that at the estimated diffusion coefficient of $1{\cdot}10^{-11}$ m^2 s^{-1}, the residence time of around 100 second is needed to expect the significant diffusion of molecules from one inflow to other outflow, as can be seen in Fig. 4. So, the symmetrical Y-shaped glass microchannel with cross-section (*w*/*d*) 220 μm × 50 μm and the entire length of the curved and smooth channel of 66 cm, supposed to be the right choice. To overcome the high pressure drop due to very high viscosity of ionic liquid and still to provide the equality of both inflows and outflows at few μL min^{-1}, the high pressure syringe pumps have to be included in experimental setup.

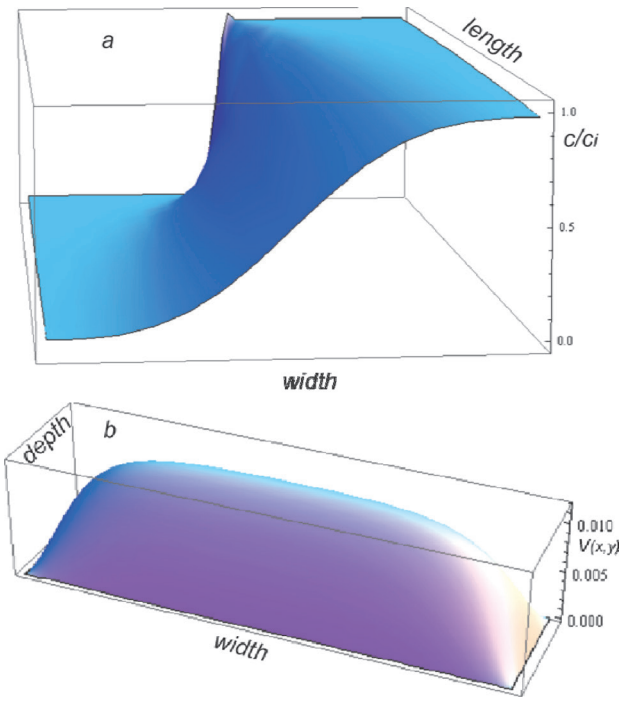

Fig. 4 – *Simulated dimensionless concentration profile (a) of molecules in IL with diffusion coefficient of $1{\cdot}10^{-11}$ m^2 s^{-1} along the microchannel with physical domain 220 μm × 50 μm × 66 cm (rectangular cross-section was used in calculations, w/d = 198.5/50 μm) at residence time of 98 s; the average percentage of molecules in both outflows is 83.5 and 16.5 %, respectively; and velocity profile (b); process conditions: flow rate of each inflow is 2 μL min^{-1} and μ = 44 mPa s*

The numerical manipulations of developed mathematical models for theoretical description of convection-diffusion dynamics are the next challenge in the determination of diffusion coefficient using a microfluidic device. It is already widely accepted that the transport phenomena in a microfluidic device can theoretically be described at macro level of description and that the continuum assumption is meaningful and valid, at least for smooth microchannels with hydraulic diameters around 100, as is the case of microchannels with typical dimensions. This was also confirmed by our report, where a very good agreement between experimental data

and macroscopic 3D model predictions is presented without any fitting procedure of model parameters.[23] More than that, the on-line validation of developed macroscopic mathematical models, ranging from a full 3D description of transport phenomena, incorporating convection, diffusion and reaction terms along with the parabolic velocity profile confirmed that the simplified less precise models assess the required model complexity for achieving precise results and to depict the governing transport characteristics at the microscale.[24] It was shown that for the majority of microfluidic studies involving forced convection, modeling can be done without considering diffusion in the direction of convection, which is in accordance with calculated Péclet numbers. Likewise, although 2D simulations assumed an infinitely deep channel, they produced identical solutions as the 3D model. Häusler *et al.*,[11] who conducted diffusion coefficient measurements in microfluidic H-cell, has proposed a simplified mass balance equation with diffusion in the transverse direction only and convection in the moving direction, where the velocity was conducted as the average velocity on simplified rectangular cross-section. In general, the simplifications of fully developed 3D models are therefore acceptable, at least for homogeneous systems. However, some important questions remain; namely, at which process conditions the specific simplifications are still reasonable, what are the estimations of error due to the model simplifications, and above all, what are the advantages of numerical solving of simplified mathematical models? Beside the validation, the verification of the proposed models still remains an essential problem of numerical analysis. Further in this work we will demonstrate some numerical procedures required for accurate determination of diffusion coefficient with microfluidic device.

When using the finite volume method, the real 3D Cartesian domain was used to define the most accurate numerical solution of governing equations (Eqs. 4–6) with appropriate boundary and initial conditions. Selected geometry of microfluidic device, described in the Experimental section, was discretized to irregular prisms (Fig. 5). The discrete volumes were smaller close to the walls and at the critical points of the microchannel, for example the Y-junction. The finite volume mesh consisted of 828000 discrete volumes. Criterion required to achieve the steady state was the initial residual of the dependent variables at a single iteration, which had to be under 10^{-4}. The steady state was in average achieved in 170 iterations for the velocity profile and 15 iterations for the concentration profiles.

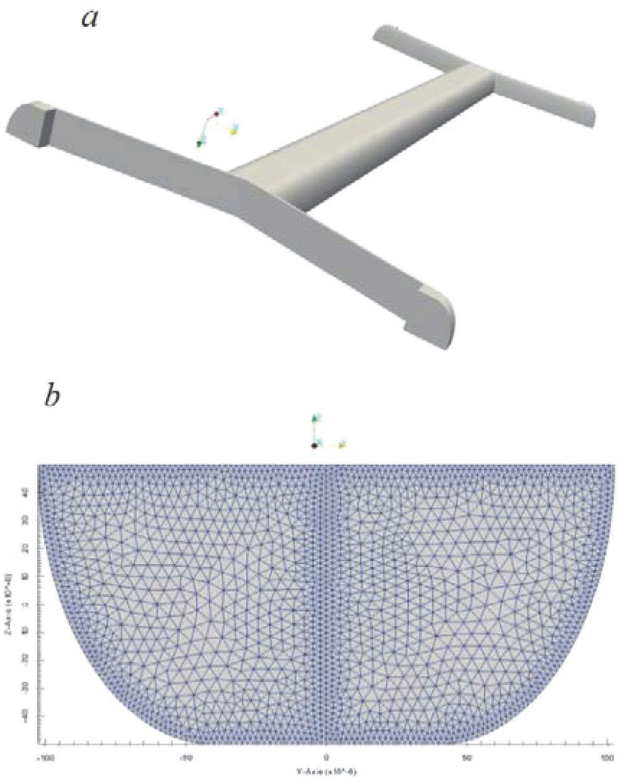

Fig. 5 – *Numerical modeling with the FVM: a) physical domain 205 μm × 100 μm × 12.5 mm; b) microchannel cross-section discretized to irregular triangles*

The same method was then used for solving the simplified system that took into account only the *z*-component of the velocity and the rectangular geometry of the channel. The approximation of curved cross-section with rectangular one was defined according to the same channel depth, as presented in Fig. 6. For the same operating and process conditions the results showed negligible deviation from the concentration profile at the outlet of the microchannel, which demonstrates and justifies the use of less complex numerical procedures and techniques to achieve an acceptable numerical accuracy of diffusion coefficient determination.

The various numerical methods based on finite volumes and finite differences, namely the explicit, implicit and Crank-Nicolson method were tested and analyzed on the same domain to predict the convection-diffusion process, theoretically described with different simplified models. While the discretization of a PDE in the form $v(x,z)C_z = D_i(C_{xx}+C_{yy}+C_{zz})$ can only be performed by implicit FDM, the discretization of a simplified form $v(x,z)$ $C_z = D_i(C_{xx}+C_{yy})$ was performed by implicit, explicit and Crank-Nicolson FDM.

As expected, all numerical approaches provided stable solutions with certain numerical variations depending on the number of iterations defined by

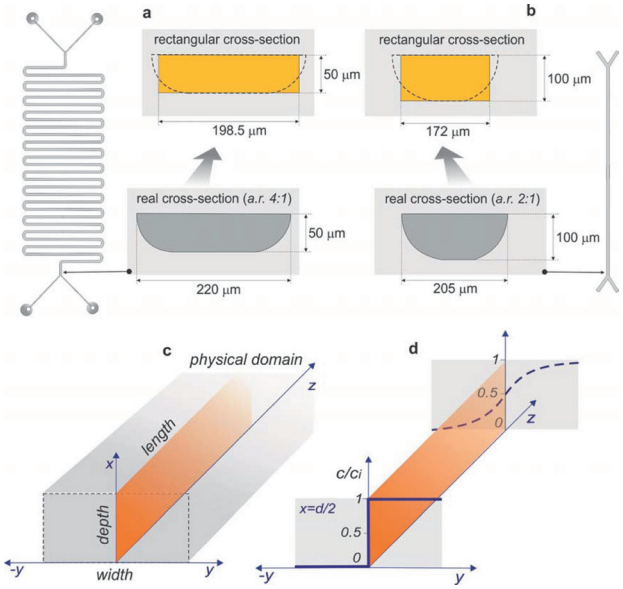

Fig. 6 – *Approximations of curved cross-sections with rectangular cross-sections at the same channel depth: a) for glass microchannel with aspect ratio 4:1 (w/d=220/50 μm); and b) for glass microchannel with aspect ratio 2:1 (w/d=205/100 μm); c) the flat "diffusion surface" in physical domain with dimension of the channel length times depth with inlet boundary condition (d)*

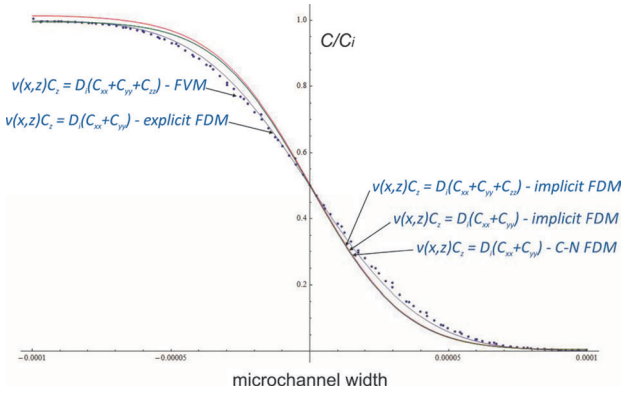

Fig. 7 – *Dimensionless concentration profiles averaged in x-direction at the exit of the microchannel – w/d = 205/100 μm →172/100 μm; process conditions: flow rate of each inflow is 20 μL min^{-1}; μ = 0. 879 mPa s; D_{AB} = 13.5·10^{-10} m^2 s^{-1}*

the mesh density (Fig. 7). Nevertheless, by applying the classical verification process it is necessary to define the optimal mesh density at which the simulation results are within acceptable error. It should be noted that the significant changes in process conditions, which appear in the model as constants or parameters require re-verification of the system. As has already been found for the theoretical description of convection-diffusion dynamics of homogeneous systems in the microfluidic device,[11,24] the simplification of the convective transport by an average velocity instead of the developed parabolic profile can be performed due to the low influence on the numerical solutions. However, a steady, fully developed Poiseuille-type flow in the microchannel can be easily determined either analytically or numerically, therefore such simplification is not proposed despite the low impact on the prediction accuracy. According to its simplicity, stability, short computation times and accuracy, of all the methods presented the explicit form of FDM is proposed for the diffusion coefficient determination of various compounds in homogeneous systems using a microfluidic device (Fig. 7).

The developed mathematical models were validated with experiments, using methylene blue in water and acetophenone in 10 % methanol aqueous solution. Methylene blue was used since it constitutes a blue solution when dissolved in water and offers the possibility to visualize the fluid flows, as well as diffusion surface, shown in Fig. 2. On the other hand, acetophenone is an interesting substrate for asymmetric synthesis of chiral amines catalyzed by omega transaminases.[25] The reaction is very difficult to carry out owing to the unfavorable thermodynamic equilibrium and severe product inhibition. In addition, acetophenone is only slightly soluble in water and for increasing its solubility a co-solvent is needed.

The determined diffusion coefficients, literature data and the corresponding estimates calculated from empirical correlations are presented in Table 2.

As evident, determined diffusion coefficient for methylene blue in water shows good agreement with the values calculated from correlations, especially with Siddiqi-Lucas correlation, which is most reliable for aqueous systems and is known to have the smallest estimated error. For acetophenone, determined diffusion coefficient shows great agreement with literature data, while deviation from the

Table 2 – *Comparison of diffusion coefficient values calculated from correlations, determined with experiments and obtained from literature*

Solute A	Solvent B	D_{AB} · 10^6 [cm^2 s^{-1}]				
		Wilke-Chang correlation	Scheibel correlation	Siddiqi-Lucas correlation	this work	literature
Methylene blue	Water	6.00	5.78	4.75	4.60	/
Acetophenone	Aqueous phosphate buffer + 10 % Methanol	8.91	8.27	/	7.35	7.66[20]

calculated values can be seen. In the case of solvent mixtures, properties of the mixture (M_B, Φ_B, V_B) need to be calculated separately, so such deviations could be anticipated.

The lack of data for solutes and solvents properties and correlations being valid for a limited number of solutes, solvents or solvent systems at specific temperatures are the main factors to embrace the microfluidic devices as a useful tool for diffusion coefficient determination. They offer the possibility to determine diffusion coefficients of various organic molecules in non-conventional solvents without needing to know their properties. Although in the case of more viscous solvents used, the dimensions regarding to the microchannel length need to be considered to ensure longer resident times needed for sufficient diffusion mass transfer.

Conclusions

Beside the advantages evident in practical applications, microspace is an environment which provides insight in the mechanism of the processes. Microfluidic devices are excellent tools to gain deeper understanding of underlying mechanism and principles like transport phenomena and kinetics. Employing this knowledge could then result in a development of a practical experimental method for gaining experimental data, which with the developed mathematical model (diffusion of one component in a homogeneous system) using the bases of continuum theory can be used to determine and evaluate mass transport or kinetic parameters. A commercially available microfluidic device with a short Y-junction microchannel was used for estimation of diffusion coefficient of methylene blue in water and acetophenone in 10 % methanol aqueous solution. For performing numerical simulations according to the simplicity, stability, short computation times and accuracy, an explicit form of FDM is proposed for determination of diffusion coefficient of various compounds in homogeneous systems using a microfluidic device. A drastic decrease of characteristic distances minimizes also the diffusion time, which then results in shorter time needed for the experiments to run. For the improvement of the developed experimental method, a continuous online measurement of the solute concentrations at the microchannel exits should be foreseen. Overall, this developed method shows capability to rapidly determine diffusion coefficient for the large variety of low molecular mass solutes in aqueous or organic solvents, while for the larger molecules and for solutes in more viscous fluids longer chips should be used.

Acknowledgments

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List of symbols

A – solute, /
$a.r.$ – aspect ratio, /
B – solvent, /
c_A – concentration of the solute A, mol L^{-1}
d – microchannel depth, m
D_{AB} – diffusion coefficient of a solute A in solvent B, $cm^2\ s^{-1}$, $m^2\ s^{-1}$
l – microchannel length, m
M_B – molecular weight of the solvent, g mol^{-1}
μ_B – solvent viscosity, mPa s
ν – kinematic viscosity, $m^2\ s^{-1}$
p – kinematic pressure, $m^2\ s^{-2}$
Φ_B – association factor of the solvent, /
T – temperature, K
$\vec{u}$ – velocity vector, m s^{-1}
V_A – molar volume of the solute at its boiling point, mL mol^{-1}
V_B – molar volume of the solvent at its boiling point, mL mol^{-1}
w – microchannel width, m
x – coordinate in the direction of channel depth
y – coordinate in the direction of channel width
z – coordinate in the direction of channel length

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