

Mutual diffusion in the ternary mixture water + methanol + ethanol and its binary subsystems

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Abstract

Mutual diffusion is investigated by means of experiment and molecular simulation for liquid mixtures containing water + methanol + ethanol. The Fick diffusion coefficient is measured by Taylor dispersion as a function of composition for all three binary subsystems at ambient conditions. For the aqueous systems, these data compare well with literature values. In case of methanol + ethanol, experimental measurements of the Fick diffusion coefficient are presented for the first time. The Maxwell-Stefan diffusion coefficient and the thermodynamic factor are predicted for the ternary mixture as well as its binary subsystems by molecular simulation in a consistent manner. The resulting Fick diffusion coefficient is compared to present measurements and to the classical simulation approach, which requires experimental vapor-liquid equilibrium or excess enthalpy data. Moreover, the self-diffusion coefficients and the shear viscosity are predicted by molecular dynamics and are favorably compared to experimental literature values. The presented ternary diffusion data should facilitate the development of aggregated predictive models for diffusion coefficients of polar and hydrogen-bonding systems.

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1 Introduction

The chemical industry has a need for accurate thermodynamic properties of mixtures in general¹. Almost all separation processes in chemical engineering, such as distillation, absorption or extraction, are affected by diffusion in liquids. Diffusion may even be the rate determining process in mass transfer unit operations² so that knowledge of the mutual diffusion coefficients is required for their design and optimization³.

To determine diffusion coefficients, experimental methods, molecular simulation, theoretical or empirical approaches are used. Numerous theoretical and empirical approaches to predict mutual diffusion coefficients in multicomponent mixtures can be found in the literature^{1,4-7}. However, these approaches often fail in predictive applications, especially when highly polar and hydrogen-bonding liquids are considered, because they relate mutual diffusion coefficients to one-component properties or simplify the interaction between unlike molecules. In this context, molecular simulation offers a promising alternative for predicting mutual diffusion coefficients.

Two rigorous descriptions of diffusive mass transport in multicomponent liquids are commonly used: generalized Fick's law and Maxwell-Stefan (MS) theory⁵. Fick's law relates a diffusive flux to a gradient of a measurable quantity, *e.g.* a mole fraction, whereas in MS theory, the driving force is the gradient of the chemical potential so that the MS diffusion coefficient is not directly accessible by experiment. The MS diffusion coefficient can be calculated by equilibrium molecular dynamics (EMD) simulation from velocity correlation functions (Green-Kubo formalism) or, alternatively, via the Einstein formalism^{5,8}. The thermodynamic factor serves as a conversion factor between both mutual diffusion coefficient types. Therefore, knowledge of the thermodynamic factor is required to determine the Fick diffusion coefficient on the basis of EMD simulation. It should be noted that the mutual diffusion coefficients and the thermodynamic factor are matrices for mixtures containing three or more components.

The thermodynamic factor is usually estimated from experimental vapor-liquid equilibrium (VLE) or excess enthalpy data^{9,10}, employing an equation of state, like Soave-Redlich-Kwong or PC-SAFT, or an excess Gibbs energy G^E model, such as Margules, Van Laar, Wilson, NRTL, UNIQUAC or UNIFAC. Some examples can be found in¹¹⁻¹⁶. However, this classical approach suffers from two drawbacks. First, the thermodynamic factor highly depends on the underlying thermodynamic model, because different G^E models may describe VLE data equally well, but yield significantly different values for the thermodynamic factor^{10,17}. The high uncertainty related to the thermodynamic factor from a thermodynamic continuum model that was regressed to VLE data has been recognized by many authors^{9,10,12,18}. Second, the thermodynamic factor determined by this approach corresponds to thermodynamic conditions under which VLE data were measured. These conditions usually differ from those where the thermodynamic factor is needed for the conversion between the mutual diffusion coefficient types.

In recent years, there has been a growing effort to obtain the thermodynamic factor directly from molecular simulation. *E.g.*, it can be estimated directly from the integration of the radial distribution function with respect to the distance using the Kirkwood-Buff theory^{19,20}. This method has some drawbacks because of the presence of strong fluctuations at large distances, thus, very large systems are required and it is difficult to obtain good statistics^{21,22}. Wedberg *et al.*²³⁻²⁵ describe a method for extending radial distribution functions that allows the Kirkwood-Buff integrals to be calculated from simulations of relatively small systems. Schnell *et al.*²⁶⁻²⁸ developed a method to compute the thermodynamic factor using

the Kirkwood-Buff integrals that were obtained from density fluctuations in small subsystems embedded in a larger simulation box using EMD simulations. They used the formalism of Hill²⁹ to obtain a finite size scaling factor, here the different boundary conditions of small periodic and non-periodic systems were accounted for by adding an effective surface energy term²⁶. This approach has been tested by Schnell *et al.*²⁶ for binary mixtures of WCA and Lennard-Jones fluids and by Liu *et al.* for the binary liquid mixtures acetone + methanol and acetone + tetrachloromethane³⁰, as well as for the ternary liquid mixture chloroform + acetone + methanol³¹.

Another molecular simulation approach is to determine the composition dependence of the chemical potential using free energy perturbation methods like Widom's particle insertion¹⁴. Recently, Balaji *et al.*³² proposed a modification of the Widom method³³ to compute the thermodynamic factor from a single simulation for mixtures of Lennard-Jones fluids.

In this work, the thermodynamic factor was calculated from the composition dependence of the chemical potential at constant temperature and pressure by Monte Carlo (MC) simulation. Because this approach is (for dense liquids) challenging with respect to the quality of molecular models, the technique used for the calculation of the chemical potential and the availability of high performance computing resources, it has often been avoided. The aim of this work is to show that the current capabilities of molecular simulation meet this challenge even for strongly polar and hydrogen-bonding liquids like aqueous alcohol mixtures.

Experiments provide the Fick diffusion coefficient on the basis of a variety of usually time consuming techniques from optical interferometry to NMR spin relaxation³⁴. The most frequently applied methods are interferometry, the diaphragm cell and Taylor dispersion, which is also known as peak broadening technique. In Taylor dispersion^{35,36}, a laminar flow of a carrier solution is pumped through a long capillary tube. A pulse of the same solution with a slightly different composition is injected. Convection and diffusion in the laminar capillary flow lead to a distortion of the peak which takes the form of a Gaussian distribution of the concentration³⁷. The Fick diffusion coefficient is calculated from the resulting concentration profile that is measured at the end of the capillary tube. This method was used in this work because it is relatively fast (1 to 3 h per experimental point) and requires a rather simple experimental set-up.

The systems under study, *i.e.* the ternary mixture water + methanol + ethanol and its binary subsystems, are highly polar hydrogen-bonding liquids, which are challenging from the point of view of both simulation and experiment. Molecular simulation results are provided for several transport properties, *i.e.* MS and Fick diffusion coefficients, self-diffusion coefficients and shear viscosity. Furthermore, experimental results for the Fick diffusion coefficient are given for all binary subsystems. In particular, experimental Fick diffusion coefficient data of methanol + ethanol are presented here for the first time.

Although binary data on the Fick diffusion coefficient are relatively abundant, experimental data on diffusion of ternary and quaternary mixtures are scarce^{13,38}, which is mainly because of experimental difficulties. Recently, Wambui Mutoru and Firoozabadi³⁸ made a literature survey on diffusion coefficient data for mixtures containing three or more components. They found experimental data points for only 94 ternary and 13 quaternary mixtures, where most of them contain water. Moreover, only data at ambient pressure and temperatures between 286 and 323 K have been reported. Unfortunately, the ternary mixture water + methanol + ethanol was not yet studied by experiment.

The number of molecular simulation studies on transport properties for complex liquids

is still low. Simulation works on mixtures containing three or more components are almost absent. Typically, aqueous solutions of methanol^{39–43} or ethanol^{22,39,43–46} have been studied by EMD simulation. Nevertheless, most of these works investigate the self-diffusion coefficient and leave aside mutual diffusion, which is more demanding than self-diffusion. For the mixture methanol + ethanol, transport properties, including the MS diffusion coefficient, were calculated in our preceding work⁴⁷. Non-equilibrium molecular dynamics simulations have also been applied to determine the shear viscosity for aqueous alcohols^{43,48,49}. However, non-equilibrium simulations are difficult to evaluate regarding diffusion, because they require very high concentration gradients beyond the linear response regime.

The success of molecular simulation to predict thermodynamic properties is primarily dependent on the molecular model that describes the intermolecular interactions. In this work, rigid, united-atom type models were used. The models for both alcohols were developed in our group^{50,51}; for water, the TIP4P/2005 model⁵² was taken from the literature. These models were tested in our previous works with respect to the binary mixtures under consideration^{39,47,48} and successfully reproduced the experimental values of transport properties in the whole composition range without a need for introducing additional parameters to adjust the interaction between unlike components. Furthermore, the TIP4P/2005 model was appreciated by many authors to be the most successful among the rigid, non-polarizable water models with respect to various structural and transport properties^{39,53–55}.

This paper is organized as follows. In section 2, the methods for the determination of the Fick diffusion coefficient from molecular simulation and experiment are described. The employed molecular models and the technical simulation details are introduced in sections 3 and 4. The experimental details are described in section 5. In section 6, results from simulation and experiment are presented and discussed. Finally, conclusions are drawn.

2 Methodology

To describe mass transport in liquid mixtures, Fick’s law and MS theory are used. Fick’s law⁵ relates a mass flux to a gradient of a driving force causing this flux. In this case, the driving force is given in terms of the gradient of a mole fraction ∇x_j . The diffusive molar flux J_i of component i is

$$J_i = -\rho \sum_{j=1}^{n-1} D_{ij} \nabla x_j, \quad i = 1 \dots n - 1, \quad (1)$$

where n is the number of components in the mixture, ρ is the molar density of the mixture and D_{ij} denotes the Fick diffusion coefficient that couples the flux of component i with the gradient of the mole fraction of component j . Because the molar fluxes depend on a choice of the reference frame, the diffusion coefficients are defined accordingly. In this work, the average molar velocity frame was used, which propagates with respect to the laboratory frame with the velocity

$$\mathbf{u} = \sum_{i=1}^n x_i \mathbf{u}_i, \quad (2)$$

where \mathbf{u}_i is the average velocity of component i in the laboratory frame. For this choice, $\sum_{i=1}^n J_i = 0$ holds. Hence, the molar flux of the reference component n is obtained from the flux balance and there are $(n-1)^2$ independent Fick diffusion coefficients.

In MS theory⁵, the driving force is the gradient of the chemical potential $\nabla\mu_i$, which is assumed to be balanced by a friction force that is proportional to the mutual velocity between the components

$$-\beta\nabla\mu_i = \sum_{j \neq i=1}^n \frac{x_j(\mathbf{u}_i - \mathbf{u}_j)}{\mathcal{D}_{ij}}, \quad (3)$$

where $\beta = 1/(k_B T)$ is the Boltzmann factor. The MS diffusion coefficient \mathcal{D}_{ij} thus plays the role of an inverse friction coefficient between components i and j . MS diffusivities are symmetric $\mathcal{D}_{ij} = \mathcal{D}_{ji}$ so that there are $n(n-1)/2$ independent MS diffusion coefficients.

Because Eqs. (1) and (3) describe the same phenomenon, a relation between both sets of diffusion coefficients exists⁵

$$\mathbf{D} = \mathbf{B}^{-1}\mathbf{\Gamma}, \quad (4)$$

in which all three symbols represent $(n-1) \times (n-1)$ matrices. \mathbf{D} is the matrix of Fick diffusion coefficients D_{ij} , the elements of the matrix \mathbf{B} are given by

$$B_{ii} = \frac{x_i}{\mathcal{D}_{in}} + \sum_{j \neq i=1}^n \frac{x_j}{\mathcal{D}_{ij}}, \quad B_{ij} = -x_i \left(\frac{1}{\mathcal{D}_{ij}} - \frac{1}{\mathcal{D}_{in}} \right), \quad (5)$$

and the so-called matrix of the thermodynamic factor $\mathbf{\Gamma}$ is defined by

$$\Gamma_{ij} = \delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,p,x_k, k \neq j=1 \dots n-1}, \quad (6)$$

where δ_{ij} is the Kronecker delta and γ_i is the activity coefficient of component i .

For binary mixtures, Eq. (4) reduces to the scalar relation

$$D = \mathcal{D}\Gamma, \quad (7)$$

because there is only a single independent MS and Fick diffusion coefficient. Here,

$$\Gamma = 1 + x_1 \frac{d \ln \gamma_1}{dx_1} = 1 + x_2 \frac{d \ln \gamma_2}{dx_2}. \quad (8)$$

The MS diffusion coefficient can be transformed to the Fick diffusion coefficient and vice versa if the thermodynamic factor is known. Only the Fick diffusion coefficient can be measured experimentally, whereas only the MS diffusion coefficient can be obtained directly from EMD simulation.

2.1 Molecular Simulation

The Fick diffusion coefficient was determined consistently by means of molecular simulation. In particular, both the MS diffusion coefficient and the thermodynamic factor were computed. As discussed above, the latter is usually derived from experimental VLE data, despite the fact that this method suffers from inaccuracies. In the present method, the thermodynamic factor was calculated straightforwardly following its definition (6). The chemical potentials, and thus the activity coefficients, were sampled by MC simulation. The derivatives of the activity coefficients at constant temperature and pressure were subsequently obtained from a fit of the simulation results using a thermodynamic model. Having the thermodynamic factor, the MS diffusion coefficients, as determined by EMD simulation, were transformed to the Fick diffusion coefficients according to Eq. (4). It will be shown that with an appropriate method and suitably chosen parameters, the composition profile of the chemical potentials can be obtained by relatively inexpensive simulations (using efficient molecular models) more plausibly than with the method based on experimental VLE data.

Transport Properties

EMD simulation and the Green-Kubo formalism^{56,57} were used here to calculate transport properties. This formalism establishes a direct relationship between a transport coefficient and the time integral of the auto-correlation function of the corresponding microscopic flux in a system under equilibrium.

For the MS diffusion coefficient, the relevant Green-Kubo expression is based on the net velocity auto-correlation function⁶

$$L_{ij} = \frac{1}{3N} \int_0^\infty dt \left\langle \sum_{k=1}^{N_i} \mathbf{v}_{i,k}(0) \cdot \sum_{l=1}^{N_j} \mathbf{v}_{j,l}(t) \right\rangle, \quad (9)$$

where N is the total number of molecules, N_i is the number of molecules of component i and $\mathbf{v}_{i,k}(t)$ denotes the velocity of k -th molecule of component i relative to the molar averaged frame of reference at a time t ⁵⁸ that was used in the definition of the Fick diffusion coefficient (2). The MS diffusion coefficient in binary mixtures is defined by⁶

$$D = \frac{x_2}{x_1} L_{11} + \frac{x_1}{x_2} L_{22} - L_{12} - L_{21}. \quad (10)$$

For a ternary mixture, the \mathbf{B}^{-1} matrix that represents the MS contribution to mutual diffusivity, *cf.* Eqs. (4) and (5), reads

$$\begin{aligned} B_{11}^{-1} &= (1 - x_1) \left(\frac{L_{11}}{x_1} - \frac{L_{13}}{x_3} \right) - x_1 \left(\frac{L_{21}}{x_1} - \frac{L_{23}}{x_3} + \frac{L_{31}}{x_1} - \frac{L_{33}}{x_3} \right), \\ B_{12}^{-1} &= (1 - x_1) \left(\frac{L_{12}}{x_2} - \frac{L_{13}}{x_3} \right) - x_1 \left(\frac{L_{22}}{x_2} - \frac{L_{23}}{x_3} + \frac{L_{32}}{x_2} - \frac{L_{33}}{x_3} \right), \\ B_{21}^{-1} &= (1 - x_2) \left(\frac{L_{21}}{x_1} - \frac{L_{23}}{x_3} \right) - x_2 \left(\frac{L_{11}}{x_1} - \frac{L_{13}}{x_3} + \frac{L_{31}}{x_1} - \frac{L_{33}}{x_3} \right), \\ B_{22}^{-1} &= (1 - x_2) \left(\frac{L_{22}}{x_2} - \frac{L_{23}}{x_3} \right) - x_2 \left(\frac{L_{12}}{x_2} - \frac{L_{13}}{x_3} + \frac{L_{32}}{x_2} - \frac{L_{33}}{x_3} \right). \end{aligned} \quad (11)$$

Beside the MS diffusion coefficient, the self-diffusion coefficient and the shear viscosity were sampled. The self-diffusion coefficient D_i^{self} is related to the mass flux of a single molecule of component i within a fluid. Therefore, the relevant Green-Kubo expression is based on the individual molecule velocity auto-correlation function⁵⁹

$$D_i^{\text{self}} = \frac{1}{3N_i} \int_0^\infty dt \sum_{k=1}^{N_i} \langle \mathbf{v}_{i,k}(t) \cdot \mathbf{v}_{i,k}(0) \rangle. \quad (12)$$

Because all molecules of a given species contribute to the self-diffusion coefficient, the auto-correlation function is averaged over all N_i molecules of component i . Thereby, a better convergence than in case of L_{ij} is achieved. This is favorable in connection with some classical predictive approaches, such as the Darken model, that estimate the MS diffusion coefficient on the basis of self-diffusion coefficients. The Darken model considers only the self-correlations in Eq. (9), resulting for binary mixtures to⁶⁰

$$\bar{D} = x_1 D_2^{\text{self}} + x_2 D_1^{\text{self}}. \quad (13)$$

Hence, the Darken model is applicable for ideally diffusing mixtures, where the contribution of the velocity cross-correlations to the net velocity auto-correlation function is negligible³⁰. Recently, Liu *et al.*⁶¹ proposed a model which requires only self-diffusion coefficients at infinite dilution to parameterize Eq. (13)

$$\frac{1}{D_i^{\text{self}}} = \sum_{j=1}^n \frac{x_j}{\lim_{x_j \rightarrow 1} D_i^{\text{self}}}. \quad (14)$$

Diffusivity is often discussed in the context of viscous properties. The shear viscosity η , as defined by Newton's "law", is associated with the momentum transport under the influence of velocity gradients. Hence, the shear viscosity can be related to the time auto-correlation function of the off-diagonal elements of the stress tensor J_p^{xy} ⁵⁹

$$\eta = \frac{\beta}{V} \int_0^\infty dt \langle J_p^{xy}(t) \cdot J_p^{xy}(0) \rangle, \quad (15)$$

where V stands for the molar volume. Averaging over all three independent elements of the stress tensor, *i.e.* J_p^{xy} , J_p^{xz} and J_p^{yz} , improves the statistics of the simulation. The component J_p^{xy} of the microscopic stress tensor \mathbf{J}_p is given by⁶²

$$J_p^{xy} = \sum_{i=1}^N m_i v_i^x v_i^y - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \sum_{a=1}^l \sum_{b=1}^m r_{ij}^x \frac{\partial u_{ij}}{\partial r_{ab}^y}. \quad (16)$$

Here, the lower indices a and b count the interaction sites and the upper indices x and y denote the spatial vector components. The index denoting a component is omitted, because the summation is carried out over all molecules regardless of their species. Finally, m_i is the mass of molecule i .

Chemical Potential

The chemical potential μ_i of component i can be separated into the solely temperature dependent ideal contribution $\mu_i^{\text{id}}(T)$ and the remaining contribution $\tilde{\mu}_i(T, p, \mathbf{x}) \equiv \mu_i(T, p, \mathbf{x}) - \mu_i^{\text{id}}(T)$. This contribution contains the desired $\ln \gamma_i$ term that appears in Eq. (6)

$$\beta \tilde{\mu}_i(T, p, \mathbf{x}) \equiv \beta \tilde{\mu}_i^\bullet(T, p) + \ln x_i + \ln \gamma_i(T, p, \mathbf{x}),$$

where \bullet denotes a pure component property. Thus, the solely temperature dependent ideal contribution does not need to be determined for the present purpose.

The composition derivative of the activity coefficient becomes

$$\left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T, p, x_k, k \neq j=1 \dots n-1} = \left. \frac{\partial (\beta \tilde{\mu}_i - \ln x_i)}{\partial x_j} \right|_{T, p, x_k, k \neq j=1 \dots n-1}. \quad (17)$$

This derivative was calculated here analytically from the Wilson model¹⁰ that was fitted to present simulation data of $\beta \tilde{\mu}_i - \ln x_i$

$$\begin{aligned} \beta \tilde{\mu}_i - \ln x_i &= \beta \tilde{M}_i + 1 - \ln S_i - \sum_{k=1}^n x_k \Lambda_{ki} / S_k, \quad i = 1 \dots n, \\ S_i &= \sum_{k=1}^n x_k \Lambda_{ik}, \quad \Lambda_{ii} = 1, \end{aligned} \quad (18)$$

where \tilde{M}_i and Λ_{ij} for $i \neq j$ are adjustable parameters. The parameter \tilde{M}_i stands for the chemical potential of the pure component i , while Λ_{ij} is related to the change of the chemical potential of component i with respect to the mole fraction of component j . The diagonal terms Λ_{ii} are constrained to be unity. In a ternary mixture, there are thus nine parameters to fit the three chemical potentials with the Wilson model: three \tilde{M}_i and six Λ_{ij} .

Inserting Eq. (18) into Eq. (6) using Eq. (17) yields the thermodynamic factor

$$\begin{aligned} \Gamma_{ij} &= \delta_{ij} + x_i(Q_{ij} - Q_{in}), \\ Q_{ij} &= -\Lambda_{ij}/S_i - \Lambda_{ji}/S_j + \sum_{k=1}^n x_k \Lambda_{ki} \Lambda_{kj} / S_k^2. \end{aligned} \quad (19)$$

Note that the thermodynamic model of a n -component mixture determines the properties of its subsystems. As a consequence, once the Wilson model for a ternary mixture is available (Eq. (18) with $n = 3$), the properties of all binary subsystems can be expressed in terms of mole fractions and the parameters of the model corresponding to the selected two components. *E.g.*, the thermodynamic factor of the binary mixture of components i and j is determined by (only two) parameters of the ternary model, *i.e.* Λ_{ij} and Λ_{ji} ,

$$\begin{aligned}
\Gamma &= 1 + x_i \frac{d \ln \gamma_i}{dx_i} = 1 + x_i(Q_{ii} - Q_{ij}) = \\
&= 1 + x_i \left(\frac{-2 + \Lambda_{ij}}{x_i + x_j \Lambda_{ij}} + \frac{\Lambda_{ji}}{x_j + x_i \Lambda_{ji}} + x_i \frac{1 - \Lambda_{ij}}{(x_i + x_j \Lambda_{ij})^2} + x_j \Lambda_{ji} \frac{\Lambda_{ji} - 1}{(x_j + x_i \Lambda_{ji})^2} \right).
\end{aligned} \tag{20}$$

2.2 Experiment

A fluid flowing through a tube develops a velocity profile which is a function of the radial position. In a fully developed laminar flow, Newtonian fluids propagate with a parabolic velocity profile. When a pulse of a solution with a different composition is injected into a laminar carrier solution flow, it propagates with the carrier flow velocity that corresponds to its position in the tube cross section⁶³. This leads to a radial concentration gradient which in turn causes radial diffusion. The molecules at the pulse front near the tube axis diffuse towards the wall into streamlines with a lower flow velocity and the molecules near the wall diffuse towards the center of the tube into streamlines with a higher flow velocity. These radial motions become important if they are of the same order of magnitude as the convective axial motion, *i.e.* when the axial flow velocity is low or the radial distances are small⁶⁴. At the end of the capillary tube, the pulse exhibits an axial Gaussian concentration profile^{35,65}.

The mathematical description of this process in binary mixtures is given by²

$$D \left[\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right] = \frac{\partial c_i}{\partial t} + U_0 \left(1 - \frac{r^2}{R^2} \right) \frac{\partial c_i}{\partial z}, \tag{21}$$

where D is the binary Fick diffusion coefficient, c_i the molarity of component i and U_0 is the velocity maximum at the center of the tube with an internal radius R . t is the time, r and z are the radial and axial coordinates, respectively.

Taylor³⁵ used a set of assumptions to find a solution for Eq. (21). He assumed that at low laminar flow rates transport via axial diffusion is small compared to the transport via convection, and that the length of the capillary tube is much larger than its diameter². When a Dirac δ -pulse is injected into the carrier solution, the shape of the dispersed pulse can then be related to a dispersion coefficient k by³⁵

$$\Delta c_i(t) = \frac{\Delta n_e}{2\pi R^2 \sqrt{\pi kt}} \exp \left[\frac{-L^2 (1 - t/\tau)^2}{4kt} \right]. \tag{22}$$

Here, $\Delta c_i(t)$ is the temporal change in concentration of component i , Δn_e is the excess number of moles present in the pulse solution when compared to the carrier solution, L is the length of the capillary tube and τ is the mean residence time. The dispersion coefficient is related to the Fick diffusion coefficient D by⁶⁵

$$k = D + \frac{R^2 L^2}{48\tau^2 D}. \tag{23}$$

If D is very small, the dispersion coefficient simplifies to³⁶

$$k = \frac{R^2 L^2}{48\tau^2 D}. \quad (24)$$

Aris⁶⁵ proposed another solution to Eq. (21) that employs the first

$$\bar{t} = \frac{\int_0^\infty dt \Delta c_i t}{\int_0^\infty dt \Delta c_i}, \quad (25)$$

and second

$$\sigma^2 = \frac{\int_0^\infty dt (t - \bar{t})^2 \Delta c_i}{\int_0^\infty dt \Delta c_i}, \quad (26)$$

moments of the concentration distribution. The Fick diffusion coefficient is then given by

$$D = \frac{R^2 \bar{t}}{24\sigma^2}. \quad (27)$$

3 Molecular Models

Throughout this work, rigid, non-polarizable molecular models of united-atom type were used. These simple models account for the intermolecular interactions, including hydrogen-bonding, by a set of Lennard-Jones (LJ) sites and point charges which may or may not coincide with the LJ site positions. The potential energy u_{ij} between two molecules i and j can thus be written as

$$u_{ij}(r_{ijab}) = \sum_{a=1}^l \sum_{b=1}^m 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ijab}} \right)^6 \right] + \frac{q_{ia}q_{jb}}{4\pi\epsilon_0 r_{ijab}},$$

where a is the site index of molecule i , b the site index of molecule j , while l and m indicate the number of interaction sites of molecules i and j , respectively. r_{ijab} represents the site-site distance between molecules i and j . The LJ size and energy parameters are σ_{ab} and ϵ_{ab} . q_{ia} and q_{jb} are the point charges located at the sites a and b of the molecules i and j , whereas ϵ_0 is the permittivity of vacuum.

For water, the TIP4P/2005 model by Abascal and Vega⁵² was used here. It consists of one LJ site and three point charges. The molecular models for methanol and ethanol were taken from prior work^{50,51} of our group. They consist of two (methanol) or three (ethanol) LJ sites and three point charges each. All models are simple, *i.e.* they do not consider internal degrees of freedom and also do not cover the polarizability in an explicit way. The interested reader is referred to the original publications⁵⁰⁻⁵² for detailed information about the three molecular pure substance models and their parameters.

To define a molecular model for a binary mixture on the basis of pairwise additive pure substance models, only the unlike interactions have to be specified. In case of polar interaction sites, *i.e.* point charges here, this can straightforwardly be done using the laws of electrostatics. However, for the unlike LJ parameters, there is no physically sound approach so that combining rules have to be employed for predictions. Here, the interactions between unlike LJ sites of two molecules were determined by the simple Lorentz-Berthelot combining rule

$$\sigma_{ab} = \frac{\sigma_{aa} + \sigma_{bb}}{2},$$

and

$$\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}}.$$

The mixture data presented below are strictly predictive, because not a single experimental data point on mixture properties or on transport properties was considered in the model parameterization.

4 Simulation Details

All simulations were carried out in a cubic volume with periodic boundary conditions. Electrostatic long-range corrections were considered by the reaction field technique with conducting boundary conditions ($\epsilon_{RF} = \infty$). The statistical uncertainties of the predicted values were estimated with a block averaging method⁶⁶.

Transport Properties

EMD simulations were performed with the program *ms2*⁶⁷. These were done in two steps: first, a simulation in the isobaric-isothermal (NpT) ensemble was carried out to calculate the density at the desired temperature, pressure and composition. Second, a canonic (NVT) ensemble simulation was carried out to determine the MS and self-diffusion coefficient as well as the shear viscosity at the temperature, composition and density from the first step.

The simulations in the NpT ensemble were equilibrated over 8×10^4 time steps, followed by a production run over 7×10^5 time steps. The NVT simulations were equilibrated over 8×10^4 time steps, followed by production runs of 9 to 14×10^6 time steps. The MS and the self-diffusion coefficients were calculated with Eqs. (10) to (12) using up to 7×10^4 independent time origins of the auto-correlation functions. The sampling length of the auto-correlation functions was 13 ps. The separation between the time origins was chosen such that all auto-correlation functions have decayed at least to $1/e$ of their normalized value to achieve their time independence⁶⁸.

In all EMD simulations, Newton's equations of motion were solved using a fifth-order Gear predictor-corrector numerical integrator with the integration time step of 0.98 fs. The temperature was controlled by velocity scaling. Here, the velocities were scaled such that the actual kinetic energy matches the specified temperature. The scaling was applied equally over all molecular degrees of freedom. The pressure was maintained using Andersen's barostat⁶⁹. The number of molecules and the cut-off radius were chosen according to our experience for

simulations of polar liquids^{39,47}. As shown there, transport properties obtained by molecular simulation may be sensitive to the system size and the cut-off radius. The cut-off was set to $r_c = 15 \text{ \AA}$ and the number of molecules was $N = 4000$. These values were also confirmed by other authors⁷⁰ to be large enough to suppress finite size effects.

Chemical Potential

Chemical potentials were calculated by MC simulations in the NVT ensemble with the program *ms2*⁶⁷. The density was determined in the NpT ensemble by EMD simulation as discussed above. The system was equilibrated over 2.5×10^4 MC moves per molecule, followed by production runs of 7.5×10^5 MC moves per molecule. Here, $N = 1024$ molecules were used and the cut-off radius was set to $r_c = 15 \text{ \AA}$.

Because the system under study is an associating liquid with a high density, Widom's test molecule insertion³³ is inappropriate to determine the chemical potential and a more complex technique has to be used. In this work, the gradual insertion method⁷¹ was employed. Instead of inserting complete test molecules, a fluctuating molecule was introduced into the simulation, which appears in different states of coupling with the other molecules. In its decoupled state, the fluctuating molecule does not interact at all with the other molecules, while in the fully coupled state, it acts like a "real" molecule of the specified component i . Between these states, a set of partially coupled states has to be defined, each with a larger fraction of the real molecule interaction.

The N real molecules plus the fluctuating molecule π_l in the state l form a set of sub-ensembles, which can be depicted by the following scheme

$$[N + \pi_0] \leftrightarrow [N + \pi_1] \leftrightarrow \dots \leftrightarrow [N + \pi_l] \leftrightarrow \dots \leftrightarrow [N + \pi_{k-1}] \leftrightarrow [N + \pi_k] . \quad (28)$$

To switch between neighboring sub-ensembles, an additional move is introduced in a standard MC simulation. The probability of accepting a change of the fluctuating molecule from a state of coupling l to a state of coupling m is given by

$$P_{acc}(l \rightarrow m) = \min \left(1, \frac{\omega_m}{\omega_l} \exp \left[-\beta(\psi_m - \psi_l) \right] \right) , \quad (29)$$

where ψ_l denotes the interaction energy of the fluctuating molecule in the state l with all other N real molecules. The states of coupling are weighted by the weighting factors ω_l to avoid an unbalanced sampling of the different states. The weighting factors were adjusted during simulation, depending on the number of times N_s the fluctuating molecule appeared in state l , according to

$$\omega_l^{new} = \omega_l^{old} \frac{N_s(k)}{N_s(l)} . \quad (30)$$

The fully coupled state k serves as a reference state for the weighting factors. Local relaxation around the fluctuating molecule was enhanced by biased translational and rotational moves in the vicinity of the fluctuating molecule throughout the simulation⁷². The chemical potential $\tilde{\mu}_i(T, p, \mathbf{x})$ of component i was then determined by

$$\beta \tilde{\mu}_i(T, p, \mathbf{x}) = \ln \left\langle \frac{N_i \omega_k}{V \omega_0} \frac{\text{Prob}[N + \pi_0]}{\text{Prob}[N + \pi_k]} \right\rangle , \quad (31)$$

where $\text{Prob}[N + \pi_0]$ and $\text{Prob}[N + \pi_k]$ are the probabilities to observe an ensemble with the fluctuating molecule in the fully decoupled and fully coupled state, respectively.

The gradual insertion method yields good results for the chemical potential in cases where Widom’s test molecule method fails. Disadvantages of the method are the extended simulation time and the additional effort needed to define the fluctuating states.

In the present simulations, six unique successive states of coupling were employed to turn on the interaction of the fluctuating molecule with the remaining molecules. These states are given in Table 1.

5 Experimental Equipment and Procedure

5.1 Apparatus

Figure 1 shows the set-up of the Taylor dispersion equipment that was employed in this work. Its design fulfills the criteria described by Alizadeh et al.⁷³. The diffusion tube was a polyetheretherketone (PEEK) capillary with a length $L = 30.945$ m and an internal diameter $2R = 0.53$ mm. The capillary was coiled around a cylinder with a radius $R_c = 0.2$ m and was placed in a thermostat (Julabo, ± 0.1 K) to maintain a specified temperature. A HPLC pump (Varian ProStar 240) with a built-in pulsation dampener was used to propagate the carrier solution in laminar flow through the dispersion tube. The part of the dispersion tube between the thermostat and the detector was also maintained at the specified temperature by shielding it with insulated tubing through which thermostat water was pumped. Zero dead volume fittings were used to connect the capillary with a six-port injection valve (Rheodyne 7725i) with an injection volume $V_{inj} = 20$ μL and with the differential refractive index (RI) detector (Varian ProStart 355 RI). This differential detector measures the difference of the refractive index between the sample stream and a liquid in a reference cell. It is equipped with a thermostatted prism and a low dead volume flow cell (6 μL). The detector was connected to a computer for digital data acquisition using the Galaxy Chromatography Software by Varian. The sampling interval of the detector was 0.2 s.

5.2 Operating Conditions

In order to investigate possible errors arising from pulsation of the HPLC pump, some test runs were carried out with a pulsation-free syringe pump. The Fick diffusion coefficient of the mixture water + ethanol at infinite dilution (pure water as a carrier) was measured for this purpose. The results from three independent measurements obtained with the syringe pump deviated by less than 1% from the results with the HPLC pump. Furthermore, no significant difference with respect to detector noise was observed. This conclusion was also reached by Van de Ven-Lucassen et al.³⁷. Subsequently, the HPLC pump was preferred, because it allows for continuous operation.

Taylor’s solution of Eq. (21) requires the composition of the injected sample to be as close as possible to the composition of the carrier. In this work, the composition difference between carrier and injected pulse solution was kept below 0.04 g/g (relative difference). The RI detector was found to have a linear response up to a mass fraction difference of 0.06 g/g, *i.e.* the measured diffusion coefficient did not show any significant dependence on the composition of the pulse solution in this range.

The influence of flow rate and capillary tube coiling on the measured Fick diffusion coefficient was examined for the two mixtures water + methanol and water + ethanol. Different experiments were carried out for flow rates from 0.05 to 0.5 mL min⁻¹. It was found that for flow rates below 0.1 mL min⁻¹, the Fick diffusion coefficient remained constant, whereas it increased above that flow rate. These erroneously high values of the Fick diffusion coefficient are most likely due to the presence of a secondary flow induced by coiling⁷⁴. Therefore, an operating flow rate of 0.05 mL min⁻¹ was chosen. As consequence, the retention time was between 7100 and 7300 s.

5.3 Experimental Procedure

Bidistilled water was used for the present experiments. Both alcohols were of analytical grade and were purchased from Sigma-Aldrich. Methanol p.a. absolute $\geq 99.8\%$ and Ethanol ACS reagent $\geq 99.5\%$ were used without further purification. The carrier solutions were prepared gravimetrically with an accuracy of ± 0.001 g. The pulse solutions were prepared volumetrically; approximately 10 mL of the carrier solution was poured into a vial, subsequently, a small amount (0.1 to 0.3 mL) of one of the components was added. After each step, the vial was weighed to determine the composition of the solution. This procedure was repeated three times for each component, giving rise to six different pulse solutions for every measured state point. When the carrier was a pure liquid, four different pulse solutions were prepared.

The carrier was allowed to flow through the Taylor apparatus for at least one day to ensure a stationary base line. The pulse solutions were then injected manually into the carrier flow. Every hour after an injection, a new sample was injected into the carrier. The time between two successive injections was chosen such that there was no overlap between the dispersion peaks of the injected pulses. Each pulse solution was injected at least three times. Hence, a total of 12 (pure carrier) or 18 measurements was carried out for each studied state point. When the carrier solution was exchanged, the apparatus was flushed for 2 h with a flow rate of 1 mL min⁻¹, before it was allowed to run overnight at the operating flow for equilibration.

The detector voltage output signal $s(t)$ was assumed to be linearly dependent on the concentration change of the flow³⁷. The base line drift of the detector was modeled using a polynomial fit of order N

$$s(t) = w\Delta c_i + \sum_{i=0}^N a_i t^i, \quad (32)$$

where w is the detector sensitivity. The data acquired by the detector was processed with a Matlab program that was complemented with a visualization tool.

The data processing program employed three different approaches to calculate the Fick diffusion coefficient from the detector signal. The numerical values of the Fick diffusion coefficient obtained from these approaches generally differed by less than 0.8%, which is below the estimated uncertainty of the Taylor dispersion method.

In the first approach, the baseline was fitted with a cubic polynomial ($N = 3$) using a least squares fit. A visual inspection of the fit was made. If it was not satisfactory, N was increased until a good fit was obtained. The base line drift was then subtracted from the detector signal. In the following step, the program localized and isolated each peak in the detector signal, *i.e.* data points having values below 5% of a peak maximum were discarded. The data points of an

isolated peak were then used to calculate the first and second moments of the concentration profile according to Eqs. (25) and (26). The corrections for the first and second moments given by Alizadeh et al.⁷³ were applied to account for errors caused by a finite injection volume and the volume of the detector cell. Finally, the Fick diffusion coefficient was calculated with Eq. (27).

The second approach followed the work of Van de Ven-Lucassen et al.³⁷. The following equation was fitted to the detector signal

$$s(t) = \frac{A}{\sqrt{\pi kt}} \exp\left[\frac{-L^2(1-t/\tau)^2}{4kt}\right] + a_1t + a_0. \quad (33)$$

Note that the baseline was modeled in this case by a linear function ($N = 1$). Here, A , k , τ , a_1 and a_0 were fitted simultaneously using a trust-region-reflective algorithm^{75,76}.

In the third approach, a three-parameter (A , k and τ) fit was carried out on the basis of data points where the base line was corrected as in case of the first approach. A visual inspection of the validity of the fit was made for every measurement. If the fit was acceptable and the Peclet number was larger than 700, Eq. (24) was employed to calculate the Fick diffusion coefficient. Otherwise, Eq. (23) was used.

The values for the Fick diffusion coefficient that are obtained with the Taylor dispersion method refer to an average composition between the composition of the carrier solution and that of the injected pulse solution. This effective concentration was calculated by⁷⁷

$$c_{i,eff} = c_{i,car} + (c_{i,inj} - c_{i,car}) \frac{V_{inj}}{2\pi R^3} \sqrt{\frac{48D}{\pi UL}}. \quad (34)$$

6 Results

6.1 Experiment

To determine the reliability of the present experimental set-up and the operating procedure, experiments were carried out for the two mixtures water + methanol and water + ethanol at 298.15 K and 1 bar. These mixtures have been studied before by other authors using the diaphragm cell⁷⁸⁻⁸² and the Taylor dispersion technique^{37,83-86}. The present results are given in Table 2. Each reported value is an average over the individual Fick diffusion coefficient measurements of the different injected samples as well as from the three different fitting approaches. The mole fraction is an average over the effective composition calculated by Eq. (34) for each injected solution. The standard deviation of the averaged values is also reported.

The present measurements are consistent with the experimental data from the literature for both mixtures at 298.15 K, *cf.* Figure 2. The average deviation of the present data to a polynomial fit of the literature data sets is in both cases $\leq 2\%$. Furthermore, the standard deviation from the observed values was also $\leq 2\%$, which is in agreement with the expected accuracy of the present measurements (2%).

In addition, new experimental data for the Fick diffusion coefficient of the mixture methanol + ethanol are listed in Table 2 and shown in Figure 2. In this case, the Fick diffusion coefficient does not exhibit a strong composition dependence, which is in contrast to the

aqueous mixtures. The Fick diffusion coefficient depends almost linearly on the mole fraction, which is evidence for an ideal solution. This finding was expected, since both alcohols are very similar in terms of their molecular interactions.

Besides the measurements at 298.15 K the isotherm 288.15 K was also considered for the mixture water + methanol. To the best of our knowledge, there are no previous measurements of the Fick diffusion coefficient for this mixture at this temperature. Figure 3 shows the present results together with the literature data at 278.15, 298.15 and 308.15 K. It can be seen that small variations of temperature strongly affect the Fick diffusion coefficient, however, the composition dependence remains almost unchanged.

The present experimental results are compared with predictions from molecular simulation and classical models in the following section.

6.2 Molecular Simulation

Predictive molecular simulations of transport properties and the thermodynamic factor of the ternary mixture water + methanol + ethanol and its binary subsystems were carried out at 298.15 K and 1 bar for various compositions as depicted in Figure 4.

The chemical potentials, which were obtained by the gradual insertion method, are listed in Table 3. The ternary Wilson G^E model, *i.e.* Eq. (18) with $n = 3$, was fitted to these data. For this purpose, the binary mixtures were treated as ternary mixtures with a vanishing mole fraction of the absent component. The parameters of the Wilson model are reported in Table 4. The resulting composition dependence of the chemical potentials is plotted in Figure 5. Figure 6 shows a comparison of the Wilson model with the original simulation data for the three binary subsystems. While the composition dependence of the chemical potentials of the mixture methanol + ethanol is well described by the ideal mixing term $\ln x_i$, the aqueous alcohols are strongly non-ideal. A comparison of the Wilson model with true ternary simulation data is given in Table 3. Obviously, the model reproduces the simulation data well.

On the basis of the Wilson model for the chemical potentials, the thermodynamic factor was computed according to Eq. (19) for the ternary mixture or Eq. (20) for the binary subsystems. For the latter case, it is compared to the thermodynamic factor obtained from experimental VLE data in Figure 7. For this purpose, recommended values for the interaction and non-randomness parameters of the Wilson model were taken (as listed in the DECHEMA Vapor-Liquid Equilibrium Data Collection⁸⁷) for 298.15 K. In addition, the thermodynamic factor resulting from a direct fit of the Wilson model to experimental VLE data⁸⁸ at 298.15 K is plotted. The mole fraction derivatives of the activity coefficients were calculated analytically using the equations given by Taylor and Kooijman¹⁰. Figure 7 shows that all three approaches give a different thermodynamic factor, except for the binary subsystem methanol + ethanol. In particular, the results based on two different parameterizations of the G^E model differ substantially. This demonstrates the general problem encountered when deriving the thermodynamic factor from experimental VLE data: although parameterizations of a G^E model may reproduce the VLE data equally well¹⁰, the differing composition derivatives may lead to a significantly differing thermodynamic factor. The fit of the chemical potential to the Wilson G^E model, introduces some systematic error to the reported thermodynamic factors. This error was estimated to be less than 5% in magnitude by comparing the thermodynamic factors reported in this work with the results using other G^E models. This shows that the present

approach suffers from model sensitivity too, though not as much the classical approach.

Figure 8 shows the MS diffusion coefficient of the three binary subsystems. The present simulation results are compared to predictions from the Darken model, Eq. (13). The self-diffusivities needed in the Darken equation were taken from experimental data or were computed by EMD simulation. Alternatively, they were predicted with the approach by Liu *et al.*, Eq. (14), which requires only data at infinite dilution. The most pronounced difference between the data sets is the apparently S-shaped slope of the simulation data for the aqueous systems, for which the other approaches lead to a convex or concave slope. Except for the mixture methanol + ethanol, the Darken model yields only a rough estimate of the MS diffusion coefficient, confirming that aqueous alcohols cannot be considered as ideally diffusing mixtures. Similarly, the prediction by Liu *et al.* fails for the aqueous binaries.

Multiplying the MS diffusion coefficient with the thermodynamic factor according to Eq. (7) leads to the Fick diffusion coefficient. To compare the present method with the method based on experimental VLE data, the MS diffusion coefficient was multiplied with the thermodynamic factor obtained from present simulations as well as from the VLE approach. In the latter case, the two parameterizations of the Wilson model were employed as discussed above, resulting in two different values of the thermodynamic factor. Figure 9 compares all respective simulation results to the present experimental data.

The present strictly predictive simulation results for the MS and the Fick diffusion coefficients as well as the thermodynamic factor are listed for the binary systems in Table 5. For the ternary mixture, the MS diffusion is given in Table 6 in terms of the \mathbf{B}^{-1} matrix, which is identical to the MS diffusion coefficient in case of binary mixtures, *cf.* Eqs. (4) and (5).

Figure 9 reveals for the aqueous binary subsystems that the present simulation method yields a smoother profile for the Fick diffusion coefficient, which qualitatively better reproduces experimental data than the classical method based on VLE data. Although both methods yield comparable deviations from the experimental data points, the profiles resulting from VLE data are flatter and exhibit a broader minimum, which is most pronounced for the case water + methanol. On the other hand, the simulation results are systematically below the experimental values. An enlarged deviation on the alcohol end of the composition range and a shift of the composition minimum are present. These drawbacks are mainly caused by deviations of pure component properties. Considering that simple molecular models were used that were fitted to static properties only and the Lorentz-Berthelot combining rule was employed to describe the interaction between unlike LJ sites, the prediction quality with respect to mutual diffusion is nonetheless remarkable.

The simulations of ternary diffusion coefficients yield consistent results. The numerical values of \mathbf{D} fulfill the theoretical restrictions for thermodynamic stability given by Taylor and Krishna⁵, *i.e.* \mathbf{D} has positive and real eigenvalues, positive diagonal elements and a positive determinant³⁸. The main term diffusion coefficient D_{ii} is larger than $D_{ij, i \neq j}$, which is expected as the diffusive flow of component i is mainly driven by its own concentration gradient⁸⁹. The coupling effects described by the cross-term diffusion coefficient D_{21} are usually smaller by one order of magnitude than D_{22} . On the other hand, the absolute numerical values of the cross-term diffusion coefficient D_{12} are important when compared to the main term D_{22} , suggesting larger coupling effects, which are typical for non-ideal mixtures. With the exception of a single state point, the cross-term D_{12} is negative. Furthermore, D_{22} is greater than D_{11} in all cases.

Unfortunately, because of the absence of experimental data on the ternary mixture, it is not possible to compare them to the present simulation results as it was done for the binary

mixtures. However, no dramatic changes in the precision of the present results for ternary mixtures when compared to the binary case are expected. The chemical potential was fitted to a unique model comprising both binary and ternary data and reproduce ternary data as good as binary ones, thus there is no loss of precision. On the other hand, the simulation uncertainty of the ternary mixtures is expected to be higher but still of the same order of magnitude than in the binary case. E.g., the Maxwell-Stefan diffusion coefficients for the ternary mixtures contain more terms than the binary ones, so their uncertainty is accordingly increased. Another factor that influence the simulation uncertainty is the reduced amount of particles for each component in the ternary case because the number of the simulated particles was kept constant.

To complete the prediction of transport properties, self-diffusion coefficients and shear viscosity are reported in Table 7 and plotted in Figures 10 and 11. The simulation results show a very good agreement with experimental data.

7 Conclusions

The Fick diffusion coefficient of the ternary mixture water + methanol + ethanol was consistently determined by equilibrium molecular simulation, *i.e.* both the MS diffusion coefficient and the thermodynamic factor were calculated by simulation on the basis of a given molecular model. The MS diffusion coefficient was sampled by EMD simulation, while the thermodynamic factor was obtained from a fit of the Wilson model to the composition profile of the chemical potentials that were directly determined by MC simulation. This method was compared for the studied binary subsystems with the classical method in which the Wilson model is regressed to experimental VLE data. As a benchmark, new experimental data for the Fick diffusion coefficient were measured by Taylor dispersion, including the mixture methanol + ethanol for which no data was previously available. For this almost ideal mixture, both simulation methods yielded very similar results and followed the experimental composition trend. However, for water + methanol and water + ethanol, the present method predicted the composition profiles qualitatively better, exhibiting pronounced minima that reflect the strong non-ideality of these systems. Furthermore, the use of classical method is limited to systems and conditions for which experimental VLE data exist, and its results vary significantly depending on which set of VLE data is used. Hence, the present simulation method is more plausible, while its agreement with experimental results is at least comparable to the classical method.

Predictive models for the MS diffusion coefficient, *i.e.* the Darken model and its simplification by Liu *et al.*, were compared to the present simulation results. For this purpose, the self-diffusion coefficients were simulated. The predictions of these models were found to be unsatisfactory for the aqueous alcohols. To complement the picture of transport properties, the shear viscosity was calculated. Similarly, as in case of the self-diffusion coefficients, the results for the shear viscosity showed a very good agreement with the experimental data from the literature.

When comparing experimental and simulative results, the experiment yields more precise data for binary mixtures (the accuracy of the Fick diffusion coefficient in present measurements is 2%). However, the use of experimental techniques for ternary diffusion measurements is hindered by serious complications, leading to the lack of experimental data in the literature. In this case, molecular simulation is an interesting alternative, since the present simulation

method does not rely on ternary experimental data and yields the ternary Fick diffusion coefficient in a similar computation time and with a similar accuracy as in the binary case.

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Table 1. Successive states used for the gradual insertion method to couple the fluctuating molecule with the system. d^*/d is the geometric factor scaling the intramolecular distances, σ^*/σ as well as ϵ^*/ϵ are the fractions of the actual LJ parameters and q^*/q is the fraction of charge magnitudes of the fully interacting molecule.

state	d^*/d	σ^*/σ	ϵ^*/ϵ	q^*/q
0	0	0	0	0
1	0.10	0.10	0.10	0
2	0.25	0.25	0.25	0
3	0.30	0.60	0.60	0.25
4	0.50	0.90	0.90	0.50
5	0.75	1.00	1.00	0.75
6	1	1	1	1

Table 2. Fick diffusion coefficient of the binary subsystems containing water (1), methanol (2) or ethanol (3) from present experiment. The numbers in parentheses indicate the standard deviation in the last digits.

x_1	x_2	x_3	D (288.15 K)	D (298.15 K)
mol mol ⁻¹	mol mol ⁻¹	mol mol ⁻¹	10 ⁻¹⁰ m ² s ⁻¹	10 ⁻¹⁰ m ² s ⁻¹
water (1) + methanol (2)				
0.998 (1)	0.002 (1)		11.87 (14)	15.23 (16)
0.800 (1)	0.200 (1)		7.84 (8)	10.31 (10)
0.601 (2)	0.399 (2)		7.21 (7)	9.20 (10)
0.502 (3)	0.498 (3)		7.69 (12)	10.20 (7)
0.401 (2)	0.599 (2)		9.19 (10)	11.83 (14)
0.220 (4)	0.780 (4)		12.67 (11)	15.85 (9)
0.008 (5)	0.992 (5)		18.29 (10)	21.06 (18)
water (1) + ethanol (3)				
0.9990 (8)		0.0010 (8)		12.37 (12)
0.899 (2)		0.101 (2)		6.61 (8)
0.750 (3)		0.250 (3)		3.83 (6)
0.594 (2)		0.406 (2)		4.11 (9)
0.506 (3)		0.494 (3)		4.92 (12)
0.459 (3)		0.541 (3)		5.54 (11)
0.291 (2)		0.709 (2)		7.78 (8)
0.189 (4)		0.811 (4)		9.60 (7)
0.008 (6)		0.992 (6)		11.65 (10)
methanol (2) + ethanol (3)				
	0.995 (3)	0.005 (3)		12.32 (10)
	0.799 (2)	0.201 (2)		13.45 (5)
	0.601 (2)	0.399 (2)		14.92 (9)
	0.501 (3)	0.499 (3)		15.60 (6)
	0.402 (3)	0.598 (3)		16.39 (7)
	0.201 (3)	0.799 (3)		18.42 (15)
	0.008 (5)	0.992 (5)		20.34 (18)

Table 3. Chemical potentials of the ternary mixture water (1) + methanol (2) + ethanol (3) and its binary subsystems from present simulations. The density ρ was chosen to yield a pressure of 1 bar at the temperature 298.15 K. The numbers in parentheses indicate the standard deviation in the last digits. The numbers in square brackets below the ternary data are the corresponding values of the present Wilson model.

x_1	x_2	x_3	ρ	$\beta\tilde{\mu}_1 - \ln x_1$	$\beta\tilde{\mu}_2 - \ln x_2$	$\beta\tilde{\mu}_3 - \ln x_3$
mol mol ⁻¹	mol mol ⁻¹	mol mol ⁻¹	mol l ⁻¹			
water (1) + methanol (2)						
1.00	0.00		55.29	-12.30 (2)		
0.95	0.05		52.41	-12.29 (2)	-8.18 (11)	
0.90	0.10		49.80	-12.32 (2)	-8.46 (9)	
0.80	0.20		45.25	-12.27 (3)	-8.72 (6)	
0.60	0.40		37.89	-12.11 (4)	-9.13 (5)	
0.40	0.60		32.33	-11.92 (4)	-9.33 (3)	
0.20	0.80		27.99	-11.73 (5)	-9.35 (2)	
0.10	0.90		26.18	-11.64 (6)	-9.34 (2)	
0.05	0.95		25.31	-11.56 (8)	-9.36 (2)	
0.00	1.00		24.54		-9.34 (4)	
water (1) + ethanol (3)						
1.00		0.00	55.29	-12.30 (2)		
0.99		0.01	54.16	-12.30 (2)		-7.71 (30)
0.90		0.10	46.13	-12.34 (3)		-8.64 (21)
0.80		0.20	39.33	-12.28 (3)		-9.43 (16)
0.60		0.40	30.00	-12.10 (3)		-9.96 (8)
0.40		0.60	24.11	-11.89 (3)		-10.04 (5)
0.20		0.80	20.08	-11.46 (5)		-10.05 (5)
0.10		0.90	18.49	-11.34 (6)		-10.06 (4)
0.01		0.99	17.24	-11.08 (15)		-10.10 (2)
0.00		1.00	17.13			-10.09 (4)
methanol (2) + ethanol (3)						
	1.00	0.00	24.54		-9.34 (4)	
	0.89	0.11	23.40		-9.37 (2)	-10.09 (7)
	0.80	0.20	22.57		-9.36 (2)	-10.09 (6)
	0.60	0.40	20.89		-9.35 (2)	-10.09 (4)
	0.40	0.60	19.47		-9.35 (3)	-10.07 (4)
	0.20	0.80	18.21		-9.38 (4)	-10.11 (4)
	0.14	0.86	17.85		-9.39 (4)	-10.13 (3)
	0.00	1.00	17.13			-10.09 (4)
water (1) + methanol (2) + ethanol (3)						
0.20	0.40	0.40	23.39	-11.61 (4)	-9.42 (2)	-10.04 (4)
				[-11.63]	[-9.39]	[-10.08]
0.40	0.20	0.40	26.37	-11.83 (3)	-9.39 (3)	-10.01 (6)
				[-11.82]	[-9.37]	[-9.95]
0.40	0.40	0.20	29.045	-11.88 (3)	-9.38 (3)	-9.99 (5)
				[-11.88]	[-9.32]	[-9.93]
0.33	0.33	0.34	26.09	-11.77 (3)	-9.37 (2)	-9.98 (5)
				[-11.78]	[-9.37]	[-9.99]

Table 4. Parameters of the Wilson model, *cf.* Eq. (18), fitted to the chemical potentials of the ternary mixture water (1) + methanol (2) + ethanol (3) and its binary subsystems from present simulations, *cf.* Table 3.

\tilde{M}_1	-12.34
\tilde{M}_2	-9.37
\tilde{M}_3	-10.13
Λ_{12}	1.02
Λ_{21}	0.22
Λ_{13}	0.80
Λ_{31}	0.10
Λ_{23}	1.01
Λ_{32}	1.03

Table 5. Maxwell-Stefan and Fick diffusion coefficients of the binary subsystems containing water (1), methanol (2) or ethanol (3) from present simulations. The density ρ was chosen to yield a pressure of 1 bar at the temperature 298.15 K. The numbers in parentheses indicate the standard deviation in the last digits.

x_1	x_2	x_3	ρ	\bar{D}	Γ	D
mol mol ⁻¹	mol mol ⁻¹	mol mol ⁻¹	mol l ⁻¹	10 ⁻¹⁰ m ² s ⁻¹		10 ⁻¹⁰ m ² s ⁻¹
water (1) + methanol (2)						
0.95	0.05		52.41	15.5 (1.2)	0.73	11.4
0.90	0.10		49.80	15.9 (1.1)	0.59	9.4
0.80	0.20		45.25	17.7 (1.7)	0.48	8.4
0.70	0.30		41.28	18.0 (1.4)	0.47	8.5
0.60	0.40		37.89	17.6 (1.9)	0.51	9.0
0.40	0.60		32.33	16.0 (1.6)	0.65	10.4
0.20	0.80		27.99	17.0 (1.7)	0.82	13.9
0.10	0.90		26.18	17.3 (1.7)	0.91	15.7
0.05	0.95		25.31	17.7 (1.8)	0.95	16.9
water (1) + ethanol (3)						
0.99		0.01	54.16	12.2 (7)	0.84	10.3
0.95		0.05	50.30	10.8 (8)	0.49	5.3
0.90		0.10	46.13	9.7 (7)	0.32	3.1
0.80		0.20	39.33	9.7 (8)	0.25	2.4
0.70		0.30	34.11	11.2 (9)	0.27	3.1
0.60		0.40	30.00	11.2 (1.0)	0.33	3.7
0.40		0.60	24.11	10.0 (1.2)	0.51	5.1
0.20		0.80	20.08	9.5 (1.1)	0.73	7.0
0.10		0.90	18.49	9.1 (1.1)	0.86	7.83
0.01		0.99	17.24	10.3 (1.1)	0.99	10.2
methanol (2) + ethanol (3)						
	0.89	0.11	23.40	21.7 (1.6)	1.01	21.8
	0.80	0.20	22.57	19.5 (2.0)	1.01	19.8
	0.60	0.40	20.89	17.1 (1.9)	1.02	17.5
	0.40	0.60	19.47	16.1 (1.4)	1.02	16.4
	0.20	0.80	18.21	15.0 (1.4)	1.01	15.2
	0.14	0.86	17.85	14.1 (1.4)	1.01	14.2

Table 6. Maxwell-Stefan and Fick diffusion coefficients of the ternary mixture water (1) + methanol (2) + ethanol (3) from present simulations. The density ρ was chosen to yield a pressure of 1 bar at the temperature 298.15 K. Note that for the 2×2 matrices \mathbf{B}^{-1} , $\mathbf{\Gamma}$ and \mathbf{D} , the reference component is ethanol.

x_1	x_2	x_3	ρ	\mathbf{B}^{-1}	$\mathbf{\Gamma}$	\mathbf{D}
mol mol ⁻¹	mol mol ⁻¹	mol mol ⁻¹	mol l ⁻¹	10 ⁻¹⁰ m ² s ⁻¹		10 ⁻¹⁰ m ² s ⁻¹
0.33	0.33	0.34	26.09	$\begin{pmatrix} 13.4 & 0.2 \\ -1.7 & 9.6 \end{pmatrix}$	$\begin{pmatrix} 0.59 & -0.10 \\ 0.14 & 1.07 \end{pmatrix}$	$\begin{pmatrix} 8.0 & -1.2 \\ 0.3 & 10.5 \end{pmatrix}$
0.20	0.40	0.40	23.39	$\begin{pmatrix} 12.1 & -0.1 \\ -0.4 & 11.7 \end{pmatrix}$	$\begin{pmatrix} 0.75 & -0.06 \\ 0.06 & 1.06 \end{pmatrix}$	$\begin{pmatrix} 9.0 & -0.9 \\ 0.4 & 12.4 \end{pmatrix}$
0.40	0.20	0.40	26.37	$\begin{pmatrix} 10.0 & -1.3 \\ -0.4 & 11.4 \end{pmatrix}$	$\begin{pmatrix} 0.52 & -0.11 \\ 0.10 & 1.06 \end{pmatrix}$	$\begin{pmatrix} 5.1 & -2.5 \\ 1.0 & 12.1 \end{pmatrix}$
0.40	0.40	0.20	29.05	$\begin{pmatrix} 12.5 & -1.0 \\ -1.6 & 11.5 \end{pmatrix}$	$\begin{pmatrix} 0.53 & -0.12 \\ 0.26 & 1.10 \end{pmatrix}$	$\begin{pmatrix} 6.3 & -2.6 \\ 2.2 & 12.9 \end{pmatrix}$
0.20	0.20	0.60	21.60	$\begin{pmatrix} 12.1 & 0.9 \\ 0.3 & 9.6 \end{pmatrix}$	$\begin{pmatrix} 0.74 & -0.06 \\ 0.01 & 1.03 \end{pmatrix}$	$\begin{pmatrix} 8.9 & 0.2 \\ 0.3 & 9.9 \end{pmatrix}$
0.20	0.60	0.20	25.48	$\begin{pmatrix} 12.9 & -1.2 \\ 0.7 & 16.2 \end{pmatrix}$	$\begin{pmatrix} 0.75 & -0.06 \\ 0.14 & 1.07 \end{pmatrix}$	$\begin{pmatrix} 9.5 & -2.1 \\ 2.8 & 17.2 \end{pmatrix}$
0.60	0.20	0.20	33.53	$\begin{pmatrix} 14.3 & -1.8 \\ -3.3 & 10.1 \end{pmatrix}$	$\begin{pmatrix} 0.34 & -0.16 \\ 0.27 & 1.10 \end{pmatrix}$	$\begin{pmatrix} 4.4 & -4.3 \\ 1.6 & 11.7 \end{pmatrix}$

Table 7. Self-diffusion coefficients and shear viscosity of the ternary mixture water(1) + methanol(2) + ethanol(3) and its binary subsystems from present simulations. The density ρ was chosen to yield a pressure of 1 bar at the temperature 298.15 K. The numbers in parentheses indicate the standard deviation in the last digits.

x_1	x_2	x_3	ρ	D_1^{self}	D_2^{self}	D_3^{self}	η
mol mol ⁻¹	mol mol ⁻¹	mol mol ⁻¹	mol l ⁻¹	10 ⁻¹⁰ m ² s ⁻¹	10 ⁻¹⁰ m ² s ⁻¹	10 ⁻¹⁰ m ² s ⁻¹	10 ⁻⁴ Pa s
water (1) + methanol (2)							
1.00	0.00		55.29	22.68 (7)			9.0 (8)
0.95	0.05		52.41	19.23 (4)	14.82 (9)		10.9 (7)
0.90	0.10		49.80	16.97 (4)	13.66 (5)		12.8 (7)
0.80	0.20		45.25	14.56 (5)	12.67 (5)		15 (1)
0.70	0.30		41.28	13.58 (4)	12.67 (4)		14.5 (8)
0.60	0.40		37.89	13.22 (5)	13.01 (5)		12.8 (9)
0.40	0.60		32.33	13.78 (4)	15.00 (3)		10.6 (5)
0.20	0.80		27.99	15.81 (7)	18.63 (4)		8.2 (4)
0.10	0.90		26.18	17.18 (9)	21.31 (4)		6.7 (3)
0.05	0.95		25.31	18.4 (1)	23.66 (4)		6.0 (3)
0.00	1.00		24.54		24.76 (7)		5.7 (4)
water (1) + ethanol (3)							
1.00		0.00	55.29	22.68 (7)			9.0 (8)
0.99		0.01	54.16	21.01 (4)		11.7 (1)	11.3 (7)
0.95		0.05	50.30	16.10 (4)		8.98 (5)	14.9 (8)
0.90		0.10	46.13	12.49 (3)		7.32 (3)	21 (1)
0.80		0.20	39.33	9.42 (3)		6.04 (2)	22 (1)
0.70		0.30	34.11	8.23 (3)		5.80 (2)	23 (1)
0.60		0.40	30.00	7.68 (3)		5.93 (2)	21 (1)
0.40		0.60	24.11	7.33 (3)		6.60 (2)	18.3 (8)
0.20		0.80	20.08	7.74 (4)		7.88 (2)	14.6 (6)
0.10		0.90	18.49	8.12 (6)		8.82 (2)	12.4 (5)
0.01		0.99	17.24	8.9 (2)		10.01 (2)	11.6 (4)
0.00		1.00	17.13			10.02 (4)	11.2 (6)
methanol (2) + ethanol (3)							
	1.00	0.00	24.54		24.76 (7)		5.7 (4)
	0.89	0.11	23.40		23.03 (6)	19.40 (9)	6.1 (4)
	0.80	0.20	22.57		21.72 (7)	18.26 (9)	5.8 (5)
	0.60	0.40	20.89		18.83 (6)	15.76 (6)	7.0 (5)
	0.40	0.60	19.47		16.08 (5)	13.36 (4)	9.5 (5)
	0.20	0.80	18.21		14.13 (6)	11.67 (4)	9.4 (6)
	0.14	0.86	17.85		13.85 (7)	11.44 (4)	9.4 (6)
	0.00	1.00	17.13			10.02 (4)	11.2 (6)
water (1) + methanol (2) + ethanol (3)							
0.33	0.33	0.34	26.09	9.96 (4)	11.50 (3)	9.16 (3)	14.8 (6)
0.20	0.40	0.40	23.39	10.72 (5)	13.08 (3)	10.63 (3)	12.3 (5)
0.40	0.20	0.40	26.37	8.84 (3)	9.84 (3)	7.83 (2)	17.0 (7)
0.40	0.40	0.20	29.05	10.89 (4)	12.03 (3)	9.49 (3)	14.0 (6)
0.20	0.20	0.60	21.60	9.05 (4)	11.26 (4)	9.15 (2)	13.3 (5)
0.20	0.60	0.20	25.48	12.87 (5)	15.54 (3)	12.65 (3)	10.1 (4)
0.60	0.20	0.20	33.53	9.83 (3)	9.77 (3)	7.48 (3)	18.1 (8)

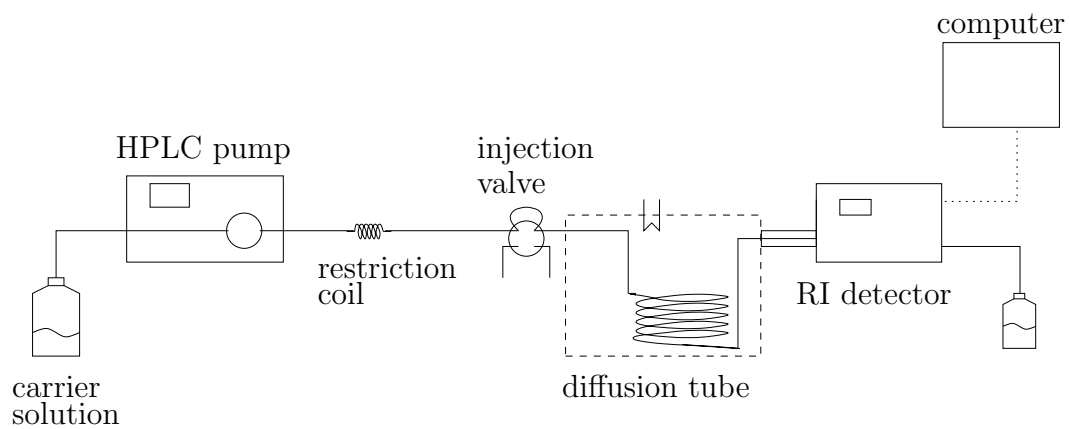


Figure 1. Experimental set-up of the Taylor dispersion measurements.

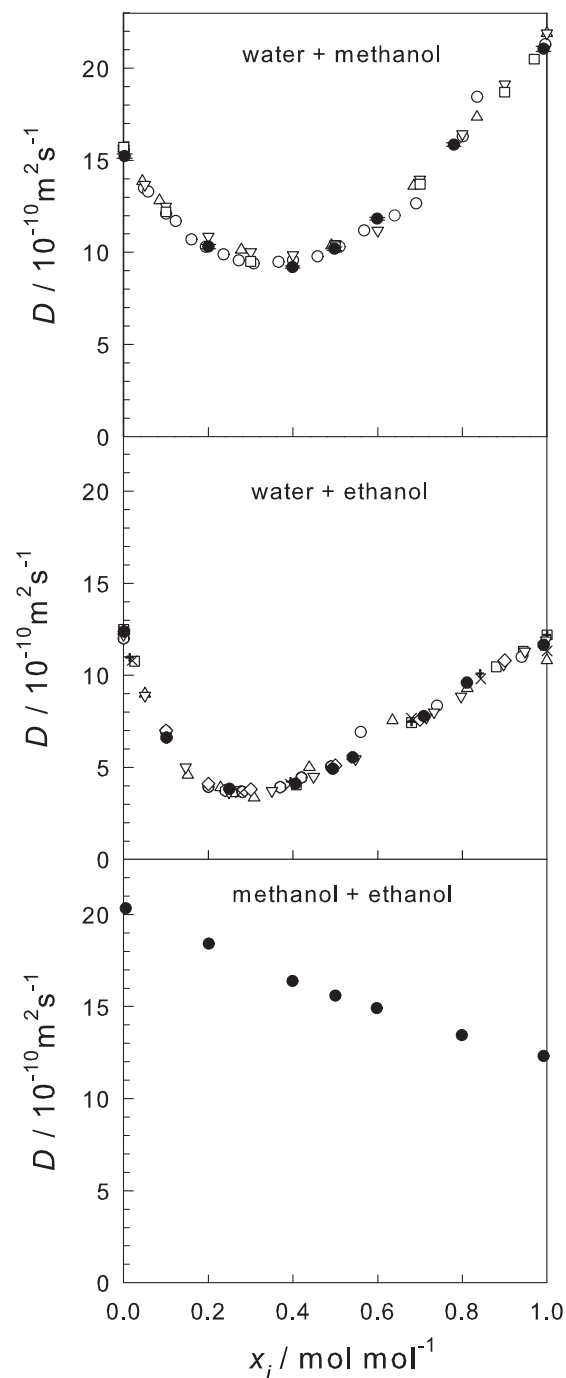


Figure 2. Fick diffusion coefficient of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component. Present experimental results (\bullet) are compared to other experimental values when available. Top: the diaphragm cell results by Derlacki et al.⁸¹ (Δ) and Woolf⁸² (∇) and the Taylor dispersion results by Van de Ven-Lucassen et al.³⁷ (\circ) and Bosse⁸⁶ (\square) are shown. Center: the diaphragm cell results by Hammond and Stokes⁷⁸ (\times), Dullien and Shemilt⁷⁹ ($+$) and Tyn and Calus⁸⁰ (\square) as well as the Taylor dispersion results by Pratt and Wakeham⁸³ (Δ), Harris et al.⁸⁴ (∇), Van de Ven-Lucassen et al.³⁷ (\circ), Hao and Leait⁸⁵ (open hexagon) and Bosse⁸⁶ (\diamond) are shown.

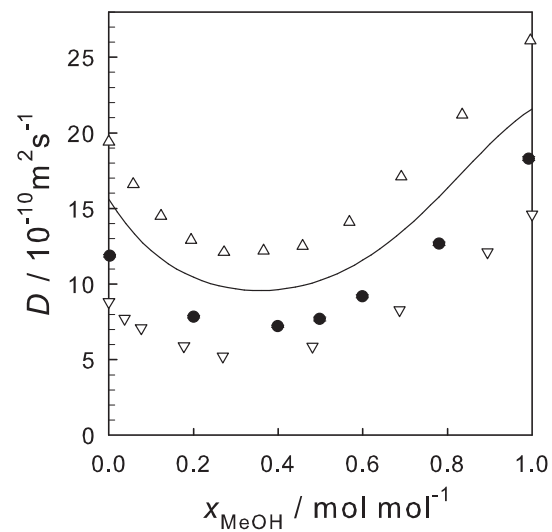


Figure 3. Temperature dependence of the Fick diffusion coefficient of water + methanol at 1 bar. Present measurements at 288.15 K (●) are shown together with a polynomial fit of various experimental data sets at 298.15 K (○). The data sets by Derlacki et al.⁸¹ at 278.15 K (▽) and Van de Ven-Lucassen et al.³⁷ at 308.15 K (△) are also shown.

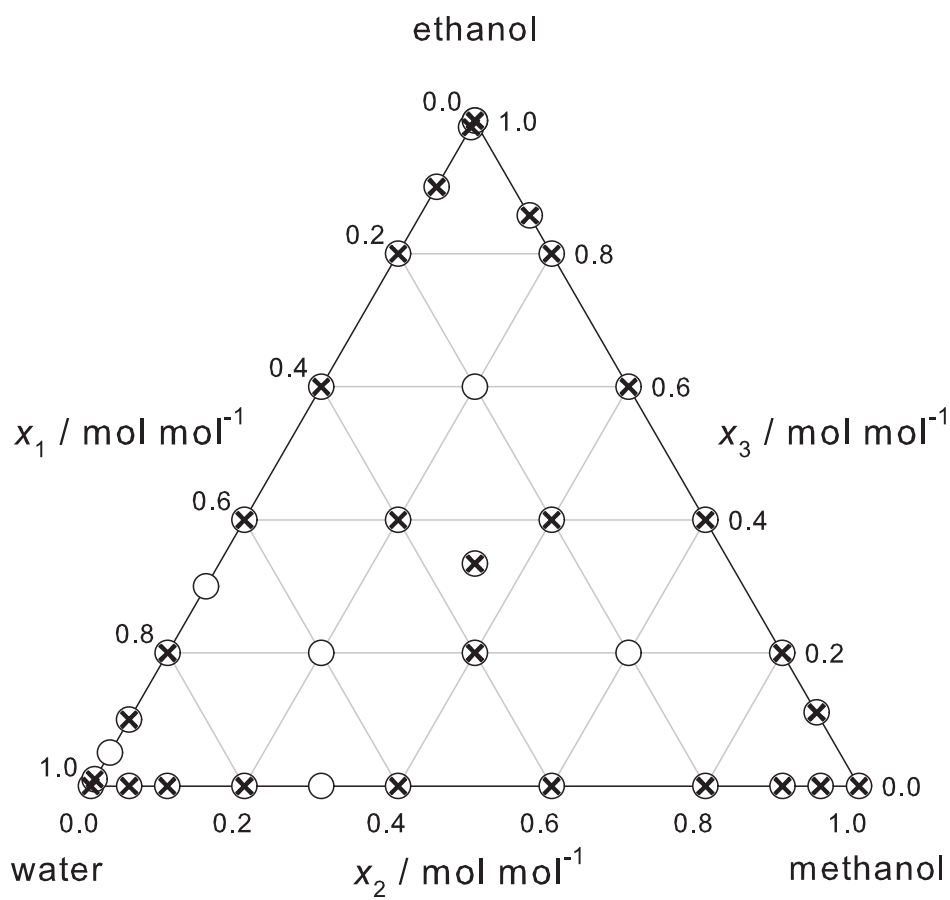


Figure 4. Compositions of the ternary mixture water (1) + methanol (2) + ethanol (3) and its binary subsystems for which the chemical potentials (\times) and the transport properties (\circ) were studied by present simulations.

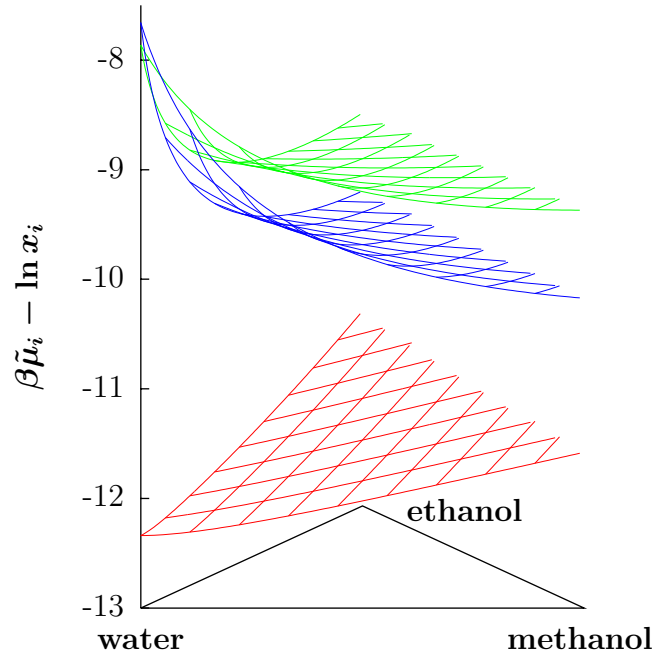


Figure 5. Chemical potential $\beta\tilde{\mu}_i - \ln x_i$ of water (bottom), methanol (center) and ethanol (top) in their ternary mixture at 298.15 K and 1 bar as a function of mole fraction. The plot is based on the ternary Wilson model, *cf.* Eq. (18), that was fitted to the present simulation results.

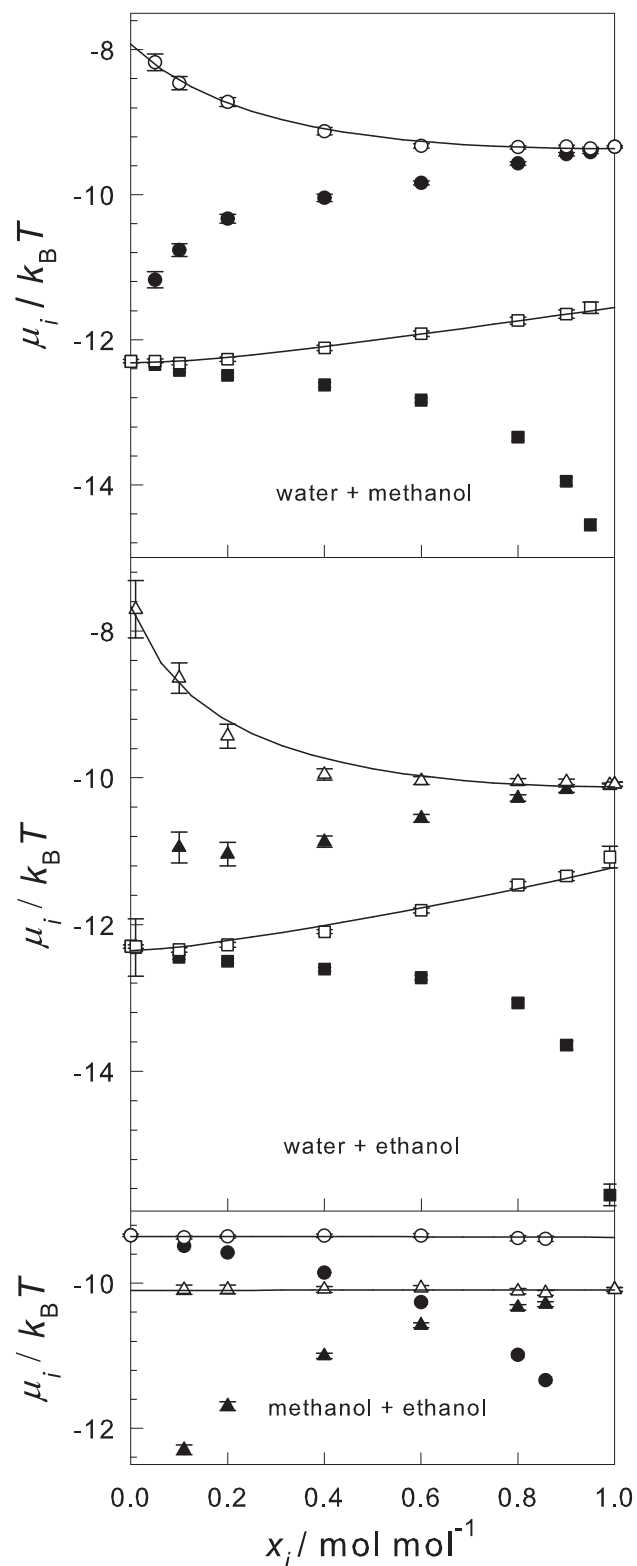


Figure 6. Chemical potentials of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component from present simulations. The chemical potentials $\beta\tilde{\mu}_i$ of water (■), methanol (●) and ethanol (▲) are denoted by full symbols. The corresponding open symbols denote the values after subtraction of ideal term: $\beta\tilde{\mu}_i - \ln x_i$. The solid line (—) shows the present ternary Wilson model.

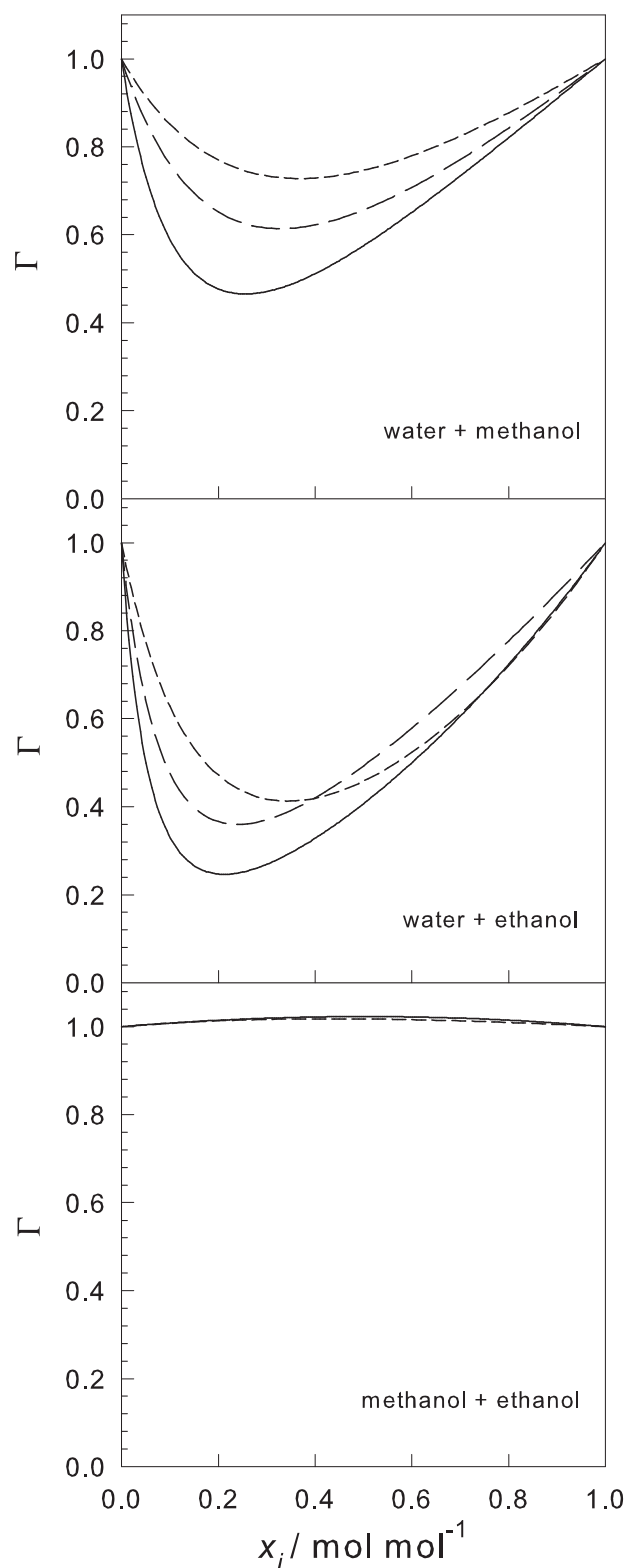


Figure 7. Thermodynamic factor of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component. The ternary Wilson model fitted to present simulation results for the chemical potentials (—) is compared to the Wilson model based on experimental VLE data with parameters recommended by DECHEMA⁸⁷ (---) for 298.15 K and to a direct fit to experimental VLE data by Hall et al.⁸⁸ at 298.15 K (-.-).

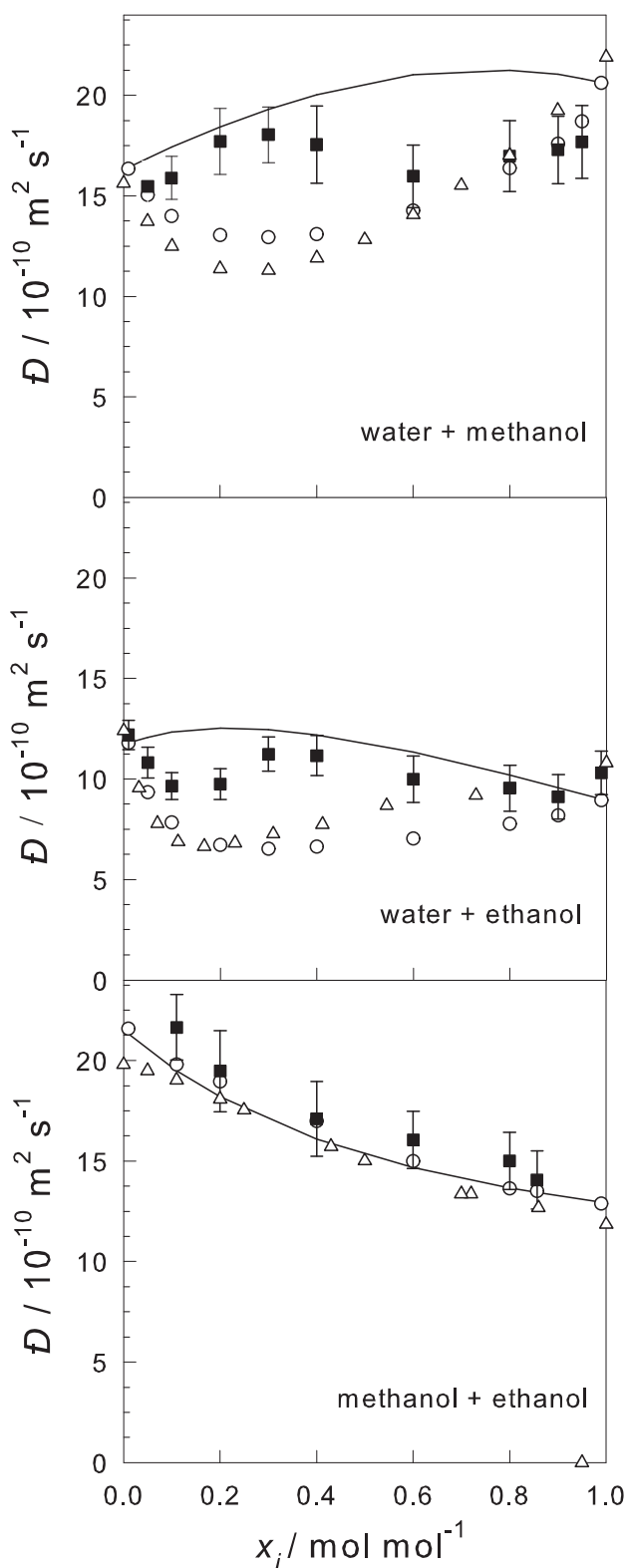


Figure 8. Maxwell-Stefan diffusion coefficient of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component. Present simulation results (■) are compared to the predictive Darken model, *cf.* Eq. (13), with experimental (Δ)^{81,90,91} and present predicted (\circ) self-diffusion coefficients, as well as with the model by Liu *et al.*⁶¹, *cf.* Eq. (14), (–).

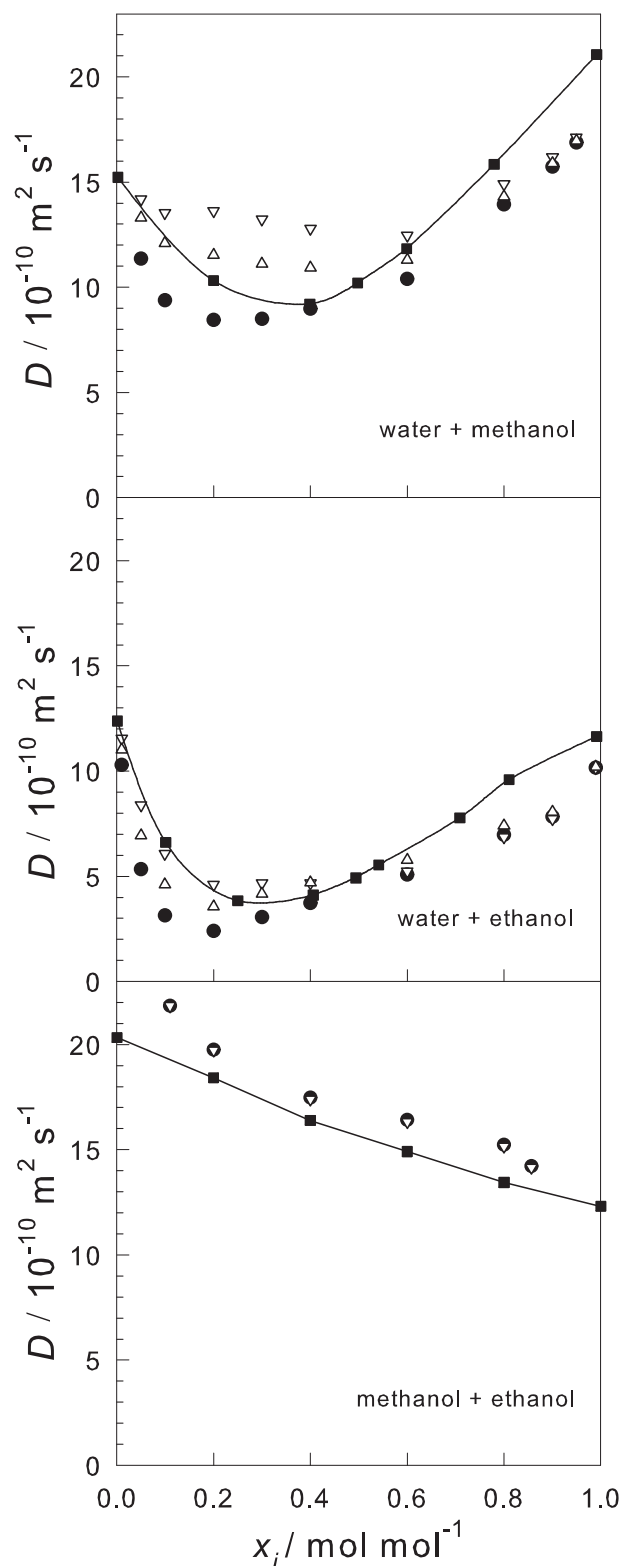


Figure 9. Fick diffusion coefficient of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component. Present simulation results (\bullet) are compared to simulation results using the thermodynamic factor from experimental VLE data (triangles) and to present experimental data from Taylor dispersion (\blacksquare). In case of the VLE data based method, the thermodynamic factor was calculated using the Wilson model with recommended parameters (\triangle) as well as by fitting it to experimental VLE data (∇) as commented in the caption of Figure 7. The straight lines serve as a guide to the eye.

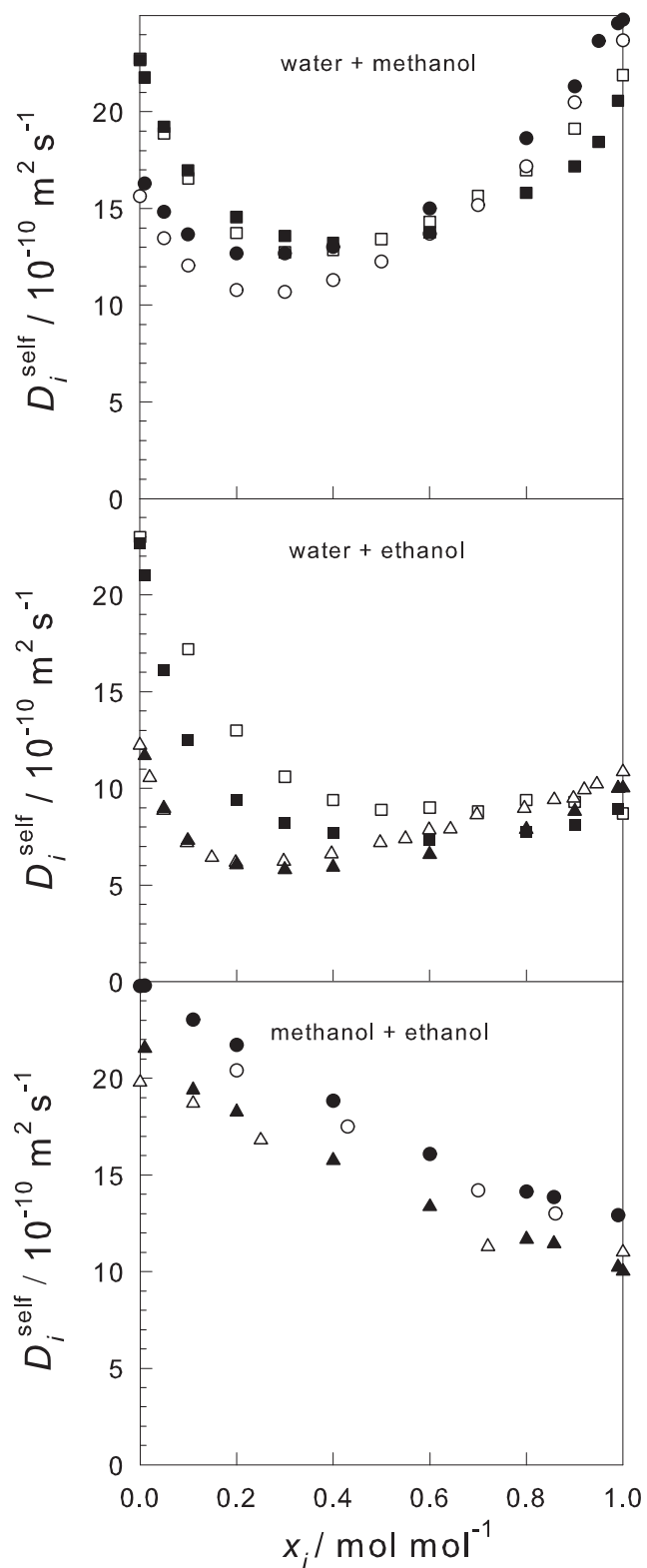


Figure 10. Self-diffusion coefficient of water (■), methanol (●) and ethanol (▲) in the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component from present simulations. The corresponding open symbols represent experimental data⁸¹ (water + methanol),^{90,92} (water + ethanol) and⁹¹ (methanol + ethanol).

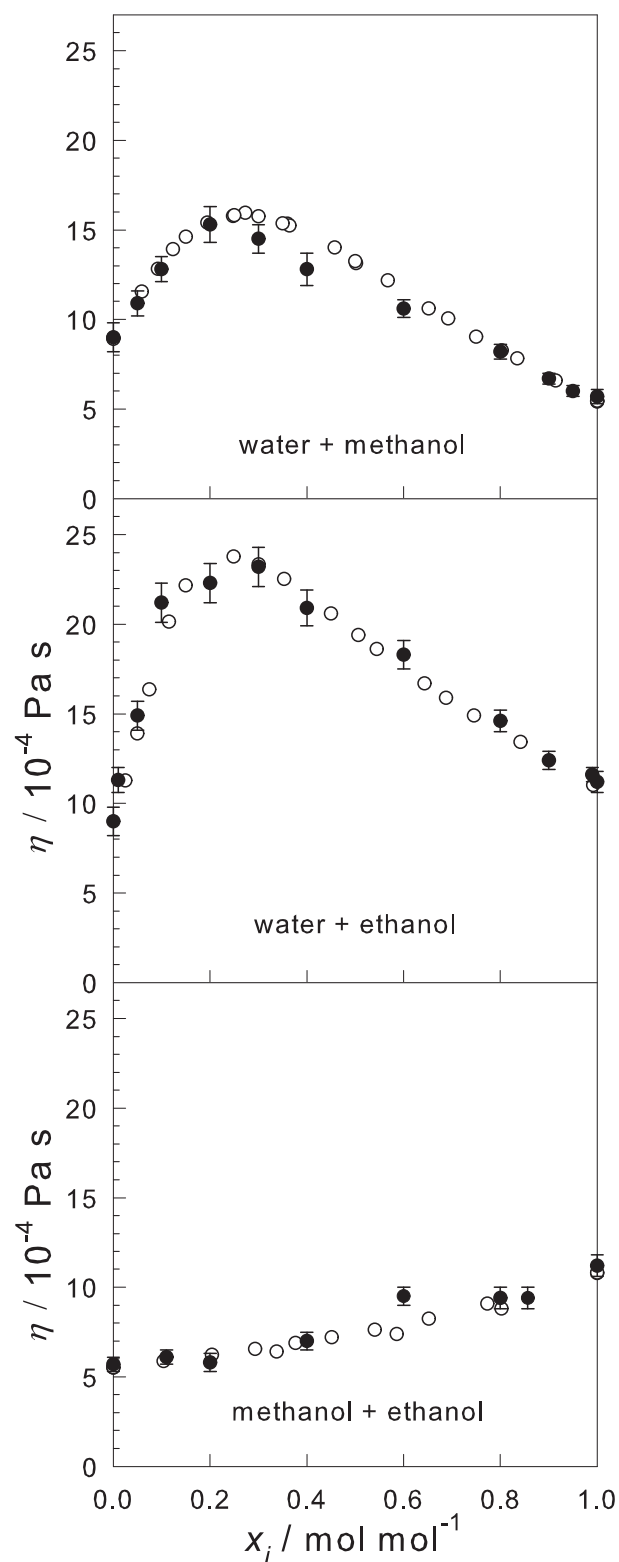


Figure 11. Shear viscosity of the binary subsystems water + methanol (top), water + ethanol (center) and methanol + ethanol (bottom) at 298.15 K and 1 bar as a function of the mole fraction of the second respective component. Present simulation results (\bullet) are compared to experimental data (\circ)^{93–95} (water + methanol),⁹⁶ (water + ethanol) and ^{97,98} (methanol + ethanol).

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