

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



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## STATE OF THE ART

Mutual diffusion plays an important role in many applications in chemistry and chemical engineering, such as distillation, absorption or liquid-liquid extraction, being often the rate limiting step.

To describe diffusive mass transport in an  $n$ -component liquid, two rigorous approaches are commonly used: generalized Fick's law and Maxwell-Stefan (MS) theory. Fick's law relates the diffusive flux  $\mathbf{J}_i$  to a gradient of a measurable quantity, e.g. a molar fraction  $x_j$ ,

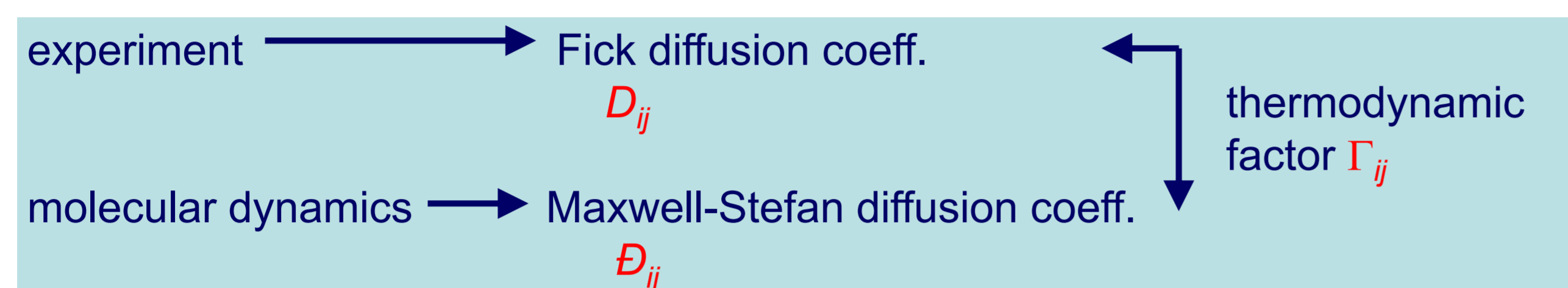
$$\mathbf{J}_i = -\rho \sum_{j=1}^{n-1} D_{ij} \nabla x_j$$

whereas in MS theory, the driving force is gradient of a chemical potential  $\mu_j$ ,

$$-\frac{\nabla \mu_i}{k_B T} = \sum_{j=1}^n \frac{x_j (\mathbf{u}_i - \mathbf{u}_j)}{D_{ij}}$$

mutual velocity of components  $i$  and  $j$

so that the MS diffusion coefficients are not directly accessible by experiment. However, the MS diffusion coefficients can be calculated by molecular dynamics (MD).



The thermodynamic factor  $\Gamma_{ij}$

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}$$

activity coefficient

serves as a conversion factor between both diffusion coefficient types

$$D = \mathcal{D} \Gamma \quad (\text{binary mixtures})$$

The thermodynamic factor is usually estimated from experimental vapor-liquid equilibrium (VLE) data employing

- equation of state (Soave-Redlich-Kwong, PC-SAFT)
- an excess Gibbs energy  $G^E$  model (Wilson, NRTL, UNIQUAC, UNIFAC)

However, this *classical* approach suffers from two drawbacks. The resulting thermodynamic factor

- is highly sensitive to the underlying thermodynamic model or the VLE data set used [1]. In fact, different  $G^E$  models may describe VLE data equally well, but yield significantly different values for the thermodynamic factor.
- corresponds to thermodynamic conditions under which VLE data were measured.

## GOAL OF CURRENT STUDIES

- 1) Determine Fick diffusion coefficients by molecular simulation in a consistent manner, i.e. compute both the MS diffusion coefficients and the thermodynamic factor from simulation data (without using VLE data).
- 2) Predict Fick diffusion coefficients for systems where other methods are unsatisfactory
  - experimental methods are hindered by serious complications for ternary and higher multicomponent mixtures
  - simulations techniques and theoretical predictive models often fail for polar hydrogen-bonding liquids

## TASK 1

### Simulation method

The MS diffusion coefficient was sampled by MD simulation using Green-Kubo expression based on the net velocity autocorrelation function

$$L_{ij} = \frac{1}{3N} \int_0^\infty dt \left\langle \sum_{k=1}^{N_i} \mathbf{v}_{ik}(0) \sum_{l=1}^{N_j} \mathbf{v}_{jl}(t) \right\rangle$$

net velocity of component  $j$  at time  $t$

The thermodynamic factor was obtained from a fit of the Wilson GE model [1] to the composition profile of the chemical potentials that were directly determined by Monte Carlo (MC) simulation. To sample chemical potentials, gradual insertion method was employed since the simple Widom method is inappropriate for dense liquids. Resulting simulation data  $m_i/k_B T - \ln x_i \equiv m_i \bullet/k_B T + \ln \gamma_i$  were fitted by the Wilson model

$$\frac{m_i \bullet}{k_B T} + \ln \gamma_i = \frac{M_i}{k_B T} + 1 - \ln S_i - \sum_{k=1}^n \frac{x_k \Lambda_{ki}}{S_k}$$

pure component chemical potential

where

$$S_i = \sum_{k=1}^n x_k \Lambda_{ik}, \quad \Lambda_{ii} = 1$$

and  $M_i$  and  $L_{ij}$  for  $i \neq j$  are the fitted parameters. The thermodynamic factor then follows from its definition.

## TASK 2

### Diffusion in alcohols

We have calculated the Fick diffusion coefficients of the ternary mixture **water + methanol + ethanol** and its **binary subsystems** at the temperature **298 K** and pressure **0.1 MPa**. The system is challenging from the point of view of both simulation (highly polar hydrogen-bonding liquid) and experiment (ternary mixture).

### Simulation details

Rigid, non-polarizable molecular models of united-atom type (LJ sites+point charges) were used [2,3,4]. Both MS diffusion coefficients and chemical potentials were sampled in NVT ensemble with density determined in an initial MD simulation at constant pressure. The total number of molecules was 4000 (for MS diffusion coefficients) or 2048 (for chemical potentials). The system was evolved for about 14 ns (MS diffusion coefficients) with timestep 1fs, or for  $7.5 \times 10^5$  MC moves per molecule (chemical potentials).

## REFERENCES

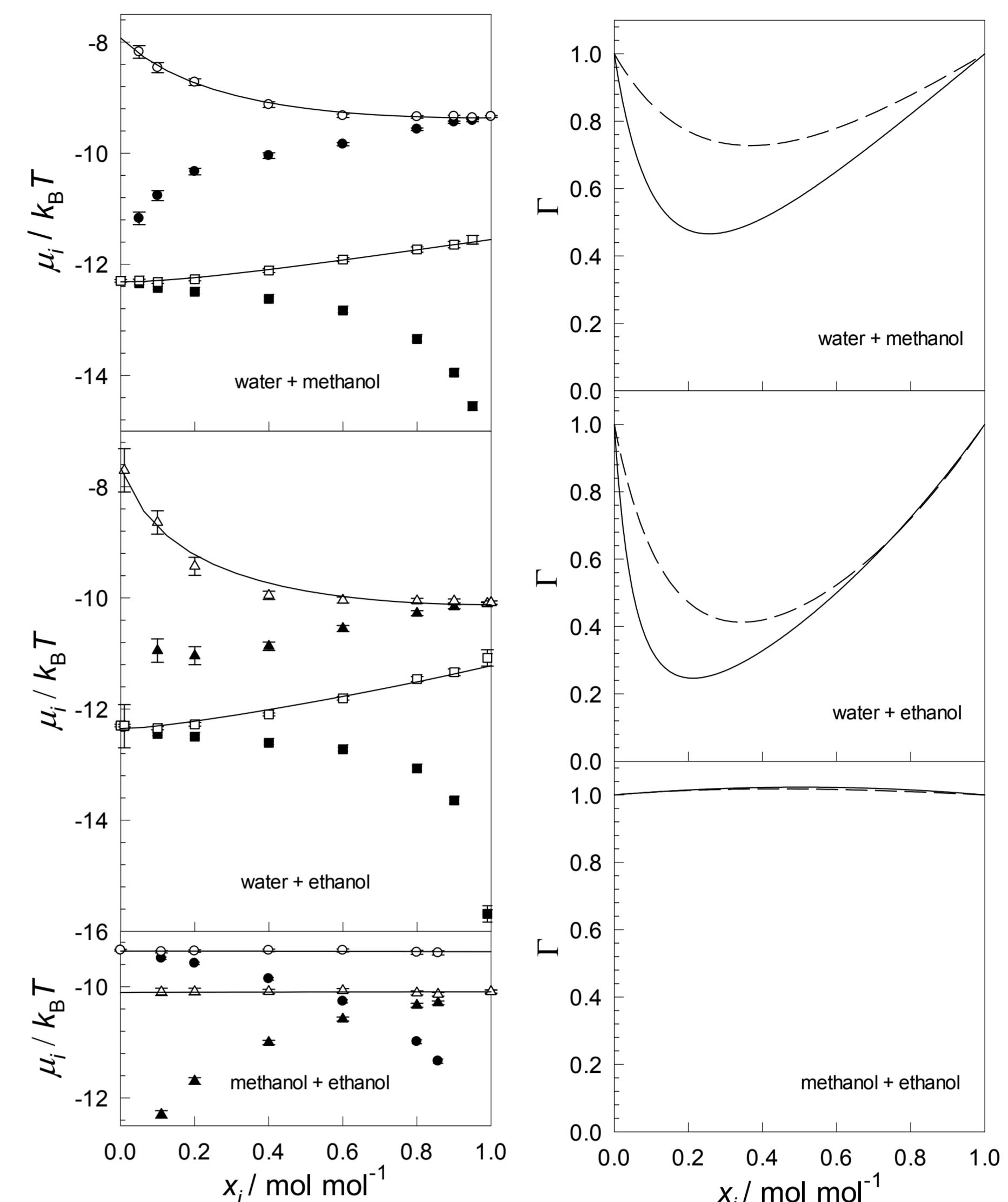
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## Results

Chemical potentials and thermodynamic factor of the three binary subsystems. Comparison with the classical method.

**Left:** Simulation results for the chemical potentials of water ( $\blacksquare$ ), methanol ( $\bullet$ ) and ethanol ( $\blacktriangle$ ). The corresponding open symbols denote the values after subtraction of logarithmic term that were fitted by the Wilson model (-).

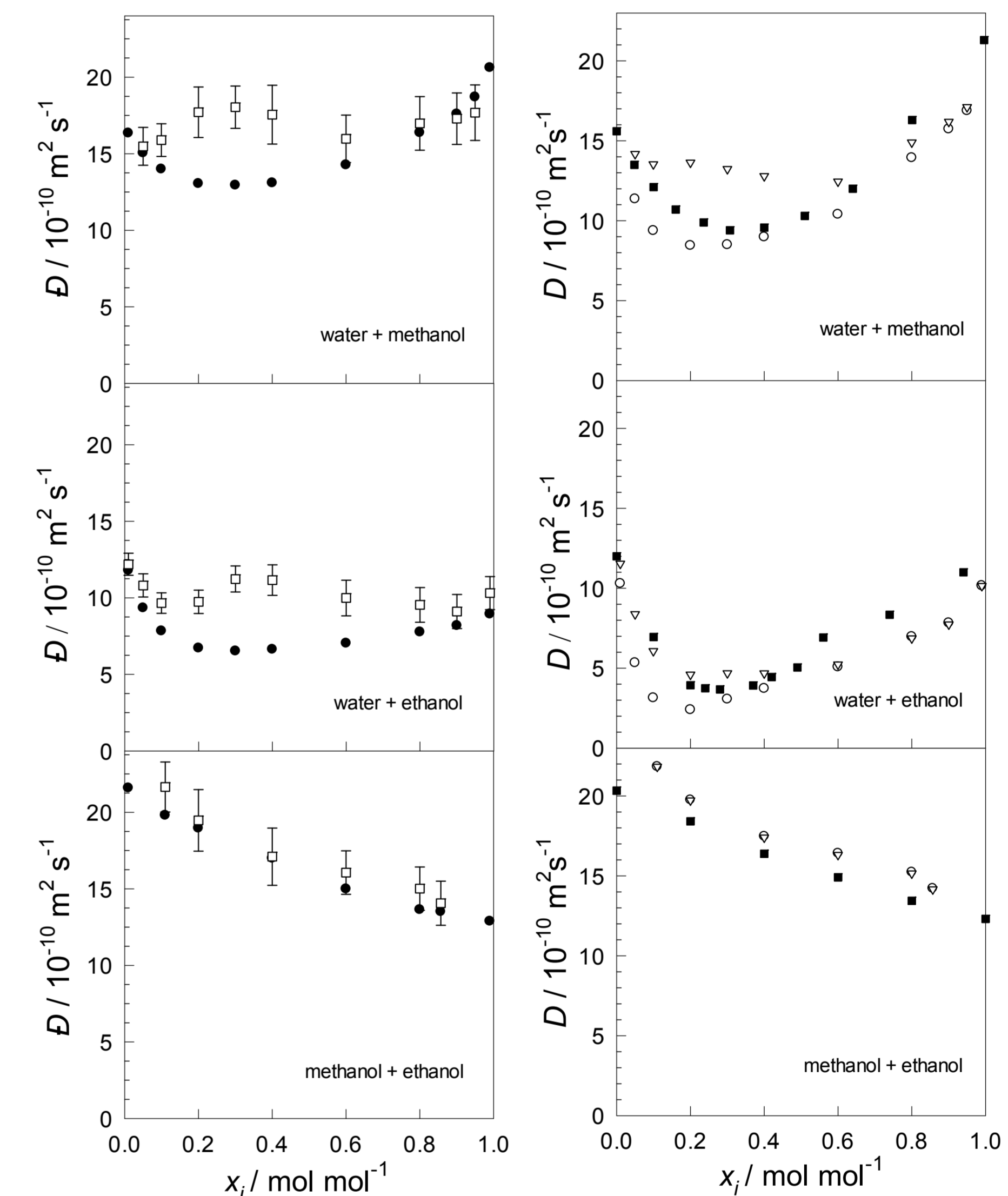
**Right:** The thermodynamic factor from present simulation data (-) and experimental VLE data [5] (---).



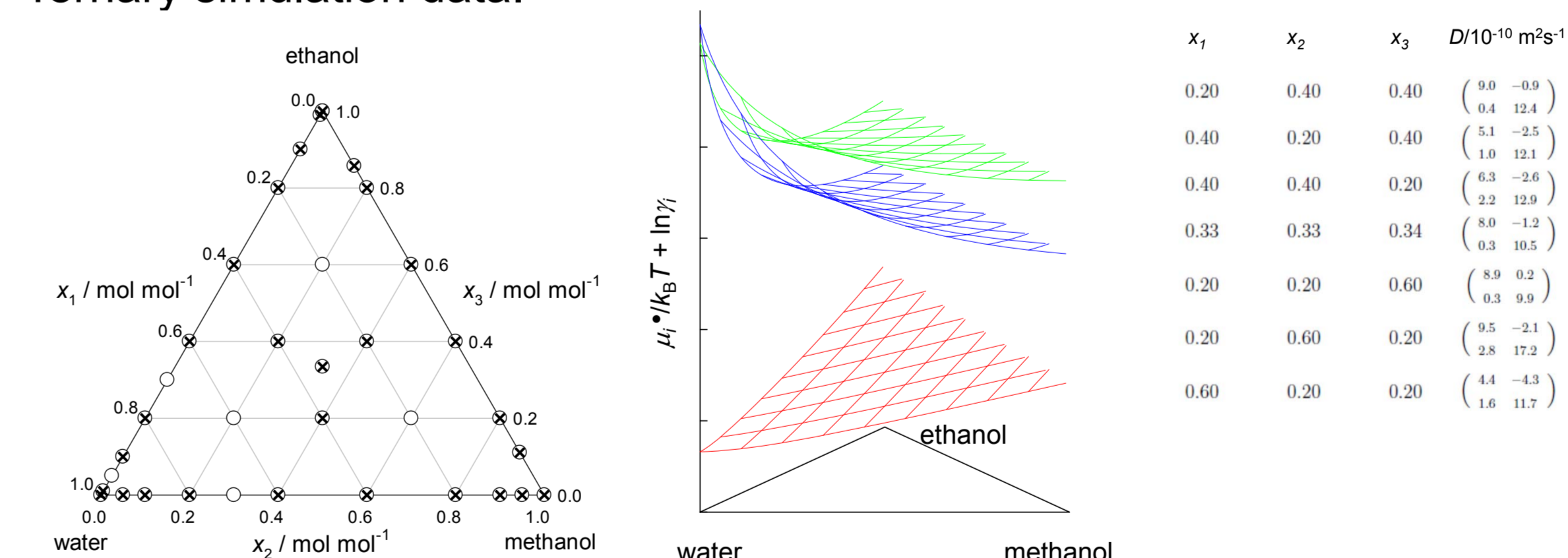
MS and Fick diffusion coefficient of the three binary subsystems. Comparison with the classical method and experiment.

**Left:** Simulation results for MS diffusion coefficient ( $\circ$ ) are compared to the Darken model ( $\bullet$ )  
 $\mathcal{D} = x_1 D_2^{self} + x_2 D_1^{self}$

**Right:** Fick diffusion coefficient from present simulation method ( $\circ$ ) and classical method [5] ( $\Delta$ ) are compared to experimental data [6,7] ( $\blacksquare$ ).



## Ternary simulation data.



**Left:** Compositions of the ternary mixture water + methanol + ethanol for which the chemical potentials ( $\times$ ) and transport properties ( $\circ$ ) were calculated.

**Center:** The Wilson model fitted to simulation data of chemical potentials.

**Right:** Simulation results for Fick diffusion coefficient.

## CONCLUSIONS

- Fick diffusion coefficients were consistently determined by equilibrium molecular simulation. No experimental VLE data were used to calculate the thermodynamic factor.
- The simulation technique is applicable even for highly polar hydrogen-bonding liquids, such as aqueous alcohols. Calculated Fick diffusion coefficients of mixtures water + methanol, water + ethanol and methanol + ethanol agree well with experimental values.
- The simulation technique is able to predict diffusion coefficients for a ternary (multicomponent) mixture where the use of experimental measurements is complicated.
- 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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