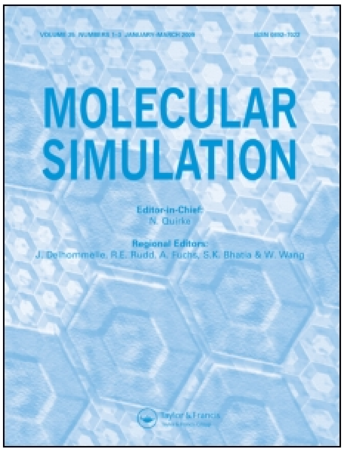

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Molecular Dynamics Simulation of Self-Diffusion and Maxwell-Stefan Diffusion Coefficients in Liquid Mixtures of Methanol and Water

Irma M. J. J. van de Ven-Lucassen[a]; Thijs J. H. Vlugt[a]; Antonius J. J. van der Zanden[a]; Piet J. A. M. Kerkhof[a]
[a] Laboratory for Separation Processes and Transport Phenomena, Eindhoven University of Technology, Eindhoven, The Netherlands

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MOLECULAR DYNAMICS SIMULATION OF SELF-DIFFUSION AND MAXWELL-STEFAN DIFFUSION COEFFICIENTS IN LIQUID MIXTURES OF METHANOL AND WATER

IRMA M. J. J. VAN DE VEN-LUCASSEN*, THIJS J. H. VLUGT,
ANTONIUS J. J. VAN DER ZANDEN and PIET J. A. M. KERKHOF

Laboratory for Separation Processes and Transport Phenomena, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Self-diffusion coefficients and Maxwell-Stefan diffusion coefficients in liquids have been determined by the equilibrium molecular dynamics calculation of the appropriate Green-Kubo equation. Simulations of water, methanol and mixtures of water and methanol have been carried out to calculate the diffusion coefficients at 300 K. In order to study the influence of the force field on the calculated self-diffusion coefficients of the pure liquids, two different force fields for each component have been used. The Van Leeuwen/Smit force field calculated the self-diffusion of methanol accurately. The SPC/E force field gave the best, but moderate, results for water. In mixtures of water and methanol the self-diffusion coefficients of both components were more accurate at high mole fractions of methanol. This can be explained by the better performance of the methanol force field. The Maxwell-Stefan diffusion coefficients in the mixtures of methanol and water agreed fairly well with the experimental values. More accurate results can be obtained by using optimised parameters in the water force field, and by enlarging the integration time and the duration of the simulation runs.

Keywords: Molecular dynamics; Green-Kubo method; self-diffusion coefficients; Maxwell-Stefan diffusion coefficients; methanol + water mixtures

1. INTRODUCTION

Diffusion in liquid systems plays an important role in chemical engineering and knowledge of diffusion coefficients is required, for example, for the

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*Corresponding author.

design of process equipment. However, in particular for mixtures it is very time consuming and difficult to measure diffusion coefficients [1, 2]. Hence, theoretical models for the estimation of the diffusion coefficients in any given system may be an attractive alternative. Simulation techniques like molecular dynamics provide a convenient method to determine the diffusion coefficients only from parameters describing the inter- and intramolecular interactions of the components of the fluid mixture.

The purpose of this study is to compute the diffusion coefficients in a methanol + water mixture. Simulations are performed on pure water, pure methanol, and on liquid mixtures of methanol + water over the entire concentration range. The results of the MD simulations are compared with experimental values from the literature. An outline of the paper is as follows. In Section 2, the main features of the theory for describing diffusion in liquids are given. The details of the simulations are described in Section 3. Section 4 presents the MD simulations of the diffusion coefficients in pure water and pure methanol, using different force fields. The MD simulations of the mixtures of water and methanol are described in Section 5.

2. THEORY

Molecular diffusion in a binary system can be described by Fick's first law:

$$J_1 = -C_t D^f_{12} \nabla x_1, \tag{1}$$

in which J_1 is the diffusion flux of component 1, C_t the total molar concentration and ∇x_1 the mole fraction gradient of component 1. D^f_{12} is the Fick diffusion coefficient. For component 2 an analogous relation can be written

$$J_2 = -C_t D^f_{21} \nabla x_2. \tag{2}$$

Because $J_1 + J_2 = 0$ and $x_1 + x_2 = 1$, it can be derived that $D^f_{12} = D^f_{21}$, *i.e.*, only one Fick diffusion coefficient describes diffusion in a binary system. Computations of diffusion coefficients from measurements are mostly performed using Fick's description of diffusion [1].

Another method for describing molecular diffusion is the Maxwell-Stefan approach. When temperature T and pressure p are constant, and when there are no external forces acting on the system, the molar fluxes N_i, N_j of components i, j due to the gradient in the chemical potential μ_i of component i are given by

$$\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{C_t D_{ij}} = \frac{x_i}{RT} \nabla_{T,p}\mu_i, \tag{3}$$

in which R is the gas constant. D_{ij} is the Maxwell-Stefan diffusion coefficient between components i and j. Because $D_{ij} = D_{ji}$, there is also only one Maxwell-Stefan diffusion coefficient describing diffusion in a binary system. The Maxwell-Stefan approach is preferred over Fick's law for describing diffusion under influence of external forces and in multicomponent systems [3].

For a binary system the Fick diffusivity D^f_{12} and the Maxwell-Stefan diffusivity D_{12} are related by

$$D^f_{12} = D_{12} \cdot \Gamma \tag{4}$$

in which Γ is the thermodynamic factor:

$$\Gamma = 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \tag{5}$$

with γ_1 is the activity coefficient of component 1. An extensive description of both methods has been given in [4].

For the calculation of Maxwell-Stefan diffusion coefficients in a binary or ternary mixture of Lennard-Jones particles an equilibrium molecular dynamics method was developed, in which the correlation function of fluctuating quantities is determined [5–8]. The integrals of the correlation functions are related to the diffusion coefficients through the Green-Kubo formalism. This so-called Green-Kubo method is preferred above a non-equilibrium method, in which the system is driven away from equilibrium and the system response is monitored [8].

The Green-Kubo method links the time correlation functions of the fluctuating quantities in an equilibrium system to the response to weak perturbations in the equilibrium system by linear response theory [9–11]. The Maxwell-Stefan diffusion coefficient D_{12} is then given by

$$D_{12} = \frac{x_2}{3n_1} \left(\frac{M_1 x_1 + M_2 x_2}{M_2 x_2} \right)^2 \int_0^\infty \left\langle \sum_{i=1}^{n_1} \mathbf{v}_1^i(0) \cdot \sum_{j=1}^{n_1} \mathbf{v}_1^j(t) \right\rangle dt \tag{6}$$

in which t is the simulation time, M_i is the molar mass of component i, n_1 the number of particles of component 1, and $\mathbf{v}_1^i$ the velocity of particle i of component 1. Calculation of the self-diffusion coefficient D_i of component i can be done simultaneously, using

$$D_i = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t)\rangle dt \tag{7}$$

The derivation of Eqs. (6) and (7) has been given in [8].

3. DETAILS OF THE SIMULATIONS

Simulations of methanol, water and mixtures of methanol + water, were carried out using the GROMOS (GRoningen MOlecular Simulation) computer package with the standard GROMOS force field [Appendix, 12, 13]. The choice of the parameter set for the GROMOS force field influences the results of the simulations. In the literature various parameter sets are described for water [14–18] and for methanol [16–21]. Those parameter values were developed to reproduce the thermodynamic properties (*e.g.*, density, energy, heat of vaporization), the structural properties, and sometimes the dynamic properties (self-diffusion coefficient) of the fluid as accurately as possible. In the simulations of this work the simple point charge (SPC) parameters and the extended SPC (SPC/E) parameters were used for the water particles. The SPC parameter set was optimised to predict the density and vaporization energy of water; the SPC/E model is a reparametrization of the SPC model to obtain the correct density and potential energy [13, 14]. For the methanol particles the standard GROMOS parameters were used as well as the parameters derived by Van Leeuwen and Smit [13, 21]. The available parameter sets for methanol, for example the GROMOS set, were optimised to predict the liquid properties at ambient temperature and pressure; only the Van Leeuwen/Smit parameter set was optimised to describe liquid coexistence densities at two temperatures and predicts the vapor–liquid curve with much higher accuracy [21]. See Table I. Note that the model of Van Leeuwen and Smit uses an Ewald summation technique for handling the long-range dipolar interactions. The GROMOS package applies a spherical cut-off, which will influence the performance of the Van Leeuwen/Smit parameter set.

Unless stated otherwise, the simulations were performed on a cubic periodic system, using a timestep of 0.002 ps and a cut-off radius $R_{\mathrm{cut}} = 0.9\,\mathrm{nm}$. After an initial energy minimisation, the system was coupled to a bath of constant temperature (300 K) with a coupling time constant $\tau_T = 0.4\,\mathrm{ps}$

TABLE I Force field parameters

	Water			*Methanol*	
	SPC	*SPC/E*		*GROMOS*	*v.Leeuwen/Smit*
$r_{O\text{-}HW1}$	0.100000	0.100000	$r_{OMet\text{-}Hmet}$	0.100000	0.100000
$r_{O\text{-}HW2}$	0.100000	0.100000	$r_{OMet\text{-}CMet}$	0.143000	0.143000
$r_{HW1\text{-}HW2}$	0.163299	0.163299	$r_{CMet\text{-}HMet}$	0.198842	0.198842
q_{OW}	−0.820	−0.8476	q_{OMet}	−0.574	−0.700
q_{HW}	0.410	0.4238	q_{HMet}	0.398	0.435
			q_{CMet}	0.176	0.265
$C_6^{1/2}(\mathrm{OW})$	0.05116	0.05116	$C_6^{1/2}(\mathrm{OMet})$	0.04756	0.04717
$C_6^{1/2}(\mathrm{HW})$	0.0	0.0	$C_6^{1/2}(\mathrm{HMet})$	0.0	0.0
			$C_6^{1/2}(\mathrm{CMet})$	0.09421	0.09783
$C_{12}^{1/2}(\mathrm{OW})$	$1.623 \cdot 10^{-3}$	$1.623 \cdot 10^{-3}$	$C_{12}^{1/2}(\mathrm{OMet})$	$1.227 \cdot 10^{-3}$	$1.3121 \cdot 10^{-3}$
$C_{12}^{1/2}(\mathrm{HW})$	0.0	0.0	$C_{12}^{1/2}(\mathrm{HMet})$	0.0	0.0
			$C_{12}^{1/2}(\mathrm{CMet})$	$4.5665 \cdot 10^{-3}$	$5.117 \cdot 10^{-3}$
R_{cut}	0.9	0.8	R_{cut}	0.9	0.9

r, R in nm; q in e; $C_6^{1/2}$ in $(\mathrm{kJ \cdot mol^{-1} \cdot nm^6})^{1/2}$; $C_{12}^{1/2}$ in $(\mathrm{kJ \cdot mol^{-1} \cdot nm^{12}})^{1/2}$
$C_6 = 4 \cdot \varepsilon \cdot \sigma^6$; $C_{12} = 4 \cdot \varepsilon \cdot \sigma^{12}$.

and equilibrated for 25,000 timesteps; a constant volume was maintained by using a coupling time constant for pressure $\tau_p = \infty$ [22]. All bond lengths were kept fixed using the SHAKE procedure with a relative tolerance of 0.0001. The pair list was updated every 5 steps. The resulting velocities and coordinates were used as a starting point for further work.

4. SIMULATIONS OF LIQUID WATER AND LIQUID METHANOL

To compare the SPC force field with the SPC/E force field in water, and the GROMOS force field with the Van Leeuwen/Smit force field in methanol, MD simulations were performed on two pure liquid systems of each force field with a box length of approximately 2.5 nm and 3.0 nm respectively. See Table II. In each system the self-diffusion coefficient and the Maxwell-Stefan diffusion coefficient using the Green-Kubo method were calculated.

4.1. Self-diffusion Coefficients

MD simulations of multiples of 1,000 timesteps were carried out in all systems. Every 1,000 timesteps a new starting value $t = 0$ was chosen and

TABLE II Self-diffusion coefficients of water and methanol, calculated with Eq. (7)

System	*Par.set*	N_{part}	*Box length**	D^*_{water}	$D^*_{methanol}$
1	SPC	509	2.50	4.9 ± 0.2	
2	SPC	898	3.02	4.7 ± 0.1	
3	SPC/E	519	2.50	3.1 ± 0.2	
4	SPC/E	889	3.00	3.45 ± 0.09	
5	meth-GR*	240	2.54		4.3 ± 0.1
6	meth-GR*	415	3.05		4.3 ± 0.1
7	meth-VL/S*	240	2.54		2.5 ± 0.1
8	meth-VL/S*	415	3.05		2.4 ± 0.1
Mills (at 25°C: 2.299) [23]				2.41	
Hurle and Woolf [26]					2.5

* box length in nm; D in $10^{-9}\,m^2 \cdot s^{-1}$; GR, GROMOS force field; VL/S, Van Leeuwen/Smit force field.

the velocity autocorrelation function $vacf(t) \equiv \langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle$ was calculated. Such a row of *vacf* data was denoted as a *vacf* set. The self-diffusion coefficient was determined by averaging over multiple *vacf* sets and integrating over 1,000 timesteps (2 ps), using Eq. (7). The accuracy of the self-diffusion coefficients was estimated by grouping the simulation data of 99 *vacf* sets into 5–10 blocks. From the standard deviation of the block averages the error in the diffusion coefficient was calculated [11]. Results are listed in Table II.

4.2. Maxwell-Stefan Diffusion Coefficients

To calculate the Maxwell-Stefan diffusion coefficients of a unary system, each system was divided into two species or components by attaching a colour label to a mole fraction x_{colour} of the particles. The two species differ only by the colour label, which plays no role in the dynamics. MD simulations of 260,000–346,500 timesteps were performed on the systems 1, 3 and 5–8. Every 10 timesteps a new time origin was taken. During the simulation the multiple particle autocorrelation function $\sum \boldsymbol{v}_1^i(0) \cdot \sum \boldsymbol{v}_1^j(t)$ was calculated for 10 different values of the mole fraction coloured component x_1 simultaneously. The Maxwell-Stefan diffusion coefficients were determined as a function of the mole fraction coloured component by integrating over 1,000 timesteps (2 ps), using Eq. (6). The accuracy of the Maxwell-Stefan diffusion coefficients was estimated by grouping the simulation data into 6–8 blocks; from the standard deviation of the block averages the error in the diffusion coefficients was calculated. Results are listed in Table III.

TABLE III Maxwell-Stefan diffusion coefficients, calculated with Eq. (6), as a function of the mole fraction coloured component for pure liquids

Water			
system 1 (*SPC*, 509 *part.*)		*system* 3 (*SPC/E*, 519 *part.*)	
x_{colour}	D^*_{MS}	x_{colour}	D^*_{MS}
0.098	4.6 ± 0.2	0.096	3.5 ± 0.3
0.196	4.3 ± 0.3	0.193	3.6 ± 0.3
0.295	4.8 ± 0.3	0.289	3.4 ± 0.3
0.393	4.9 ± 0.3	0.385	3.5 ± 0.2
0.491	5.1 ± 0.3	0.482	3.6 ± 0.2
0.589	4.7 ± 0.4	0.578	4.1 ± 0.3
0.688	4.9 ± 0.5	0.674	3.9 ± 0.3
0.786	4.7 ± 0.4	0.771	3.4 ± 0.2
0.884	5.6 ± 0.3	0.867	3.3 ± 0.2
0.982	5.2 ± 0.4	0.963	3.8 ± 0.2
Methanol			
system 5 (*meth-GR*, 240 *part.*)		*system* 6 (*meth-GR*, 415 *part.*)	
x_{colour}	D^*_{MS}	x_{colour}	D^*_{MS}
0.083	4.3 ± 0.2	0.096	4.4 ± 0.3
0.167	4.6 ± 0.5	0.193	4.5 ± 0.6
0.250	4.0 ± 0.4	0.289	4.2 ± 0.4
0.333	3.9 ± 0.3	0.386	4.1 ± 0.4
0.417	4.1 ± 0.5	0.482	4.2 ± 0.5
0.500	4.3 ± 0.4	0.578	4.7 ± 0.4
0.583	4.2 ± 0.4	0.675	4.6 ± 0.3
0.667	4.0 ± 0.6	0.771	4.8 ± 0.4
0.750	4.1 ± 0.5	0.867	4.5 ± 0.3
0.833	4.6 ± 0.2	0.964	4.4 ± 0.2
system 7 (*meth-VL/S*, 240 *part.*)		*system* 8 (*meth-VL/S*, 451 *part.*)	
x_{colour}	D^*_{MS}	x_{colour}	D^*_{MS}
0.083	2.5 ± 0.3	0.096	2.7 ± 0.5
0.167	2.7 ± 0.2	0.193	3.1 ± 0.7
0.250	3.0 ± 0.2	0.289	3.6 ± 1.0
0.333	2.8 ± 0.1	0.386	2.9 ± 0.6
0.417	2.5 ± 0.2	0.482	2.6 ± 0.7
0.500	2.6 ± 0.3	0.578	3.3 ± 0.7
0.583	2.6 ± 0.2	0.675	3.1 ± 0.8
0.667	2.7 ± 0.2	0.771	3.3 ± 0.8
0.750	2.6 ± 0.2	0.867	3.1 ± 0.6
0.833	2.5 ± 0.2	0.964	2.5 ± 0.4

* D_{MS} in $10^{-9}\ m^2 \cdot s^{-1}$.

4.3. Comparison of the Force Fields

Tables II and III show a better performance of the SPC/E parameter set in water. The self-diffusion coefficient of the SPC/E model is closer to the experimental value of Mills [23, 24] than the SPC value, with comparable standard deviations. Simulations of Berendsen *et al.* [14] also showed an improvement of the value of the self-diffusion coefficient from $4.3 \cdot 10^{-9}\ m^2 \cdot s^{-1}$

using the SPC parameters to $2.5 \cdot 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ using the SPC/E parameters; the SPC/E value was even within simulation error of the experimental value. However, Caldwell and Kollman [17] could not obtain this value in non-additive MD simulations using their polarizable model with the SPC/E parameters, and calculated a self-diffusion coefficient of $3.1 \cdot 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$. The simulations of Berendsen *et al.*, as well as the simulations of Caldwell and Kollman were performed on a cubic box of 216 particles. An influence of the system size on the calculation of the self-diffusion coefficient might explain the differences between the results of the simulations of both Berendsen *et al.*, and Caldwell and Kollman and the results of our simulations given in Table II [25]. Since the SPC/E model agreed best with the experimental data, we decided to use this model for further work.

Tables II and III show a good performance of the Van Leeuwen/Smit parameter set in methanol. The self-diffusion coefficient is in good agreement with the value $2.50 \cdot 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ from the literature [26]. The Van Leeuwen/Smit parameter set also performs better than the polarizable model of Caldwell and Kollman, which gives a value of $2.65 \cdot 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ [17], and than the refinements of Jorgensen (parameter sets J1 and J2), and Haughney (parameter sets H1 and H2) of the three-site united-atom approach for the intermolecular potential of Jorgensen tested by Haughney *et al.* [20]. Casulleras and Guardia used the J2 model for their simulations of liquid methanol at 298 K, in which they studied the effect of the system size on the transport properties and the structure of liquid methanol [25]. The self-diffusion coefficient D_m of methanol increased from $D_m = 2.23 \cdot 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ to $D_m = 2.59 \cdot 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ with increasing number of particles N from $N = 125$ to $N = 512$. The Van Leeuwen/Smit model was constant within the simulation error (Tab. II). Therefore, for further work the Van Leeuwen/Smit parameter set was used for methanol.

The Maxwell-Stefan diffusion coefficients in the pure liquids, shown in Table III, agree fairly well with the self-diffusion coefficients, shown in Table II, but are less accurate. This is in accordance with the results of the simulations performed for Lennard-Jones systems by Van de Ven-Lucassen *et al.* [8]. Increasing the integration time and the simulation time might improve the accuracy of the Maxwell-Stefan diffusion coefficients.

5. SIMULATIONS OF MIXTURES OF WATER AND METHANOL

Simulations were performed on 10 systems of methanol + water particles at 300 K and 1 atm. (Tab. IV). In the systems with a mole fraction of methanol

TABLE IV Self-diffusion coefficients of methanol and water in methanol + water mixtures, calculated with Eq. (7)

$N_{methanol}$	N_{water}	*density**	*Box length**	$x_{methanol}$	$D^*_{methanol}$	D^*_{water}
80	744	977	3.006	0.097	1.69 ± 0.11	2.55 ± 0.7
150	596	955	3.001	0.201	1.58 ± 0.05	1.96 ± 0.05
200	499	937	3.011	0.286	1.41 ± 0.03	1.80 ± 0.03
250	385	914	3.006	0.394	1.28 ± 0.04	1.75 ± 0.04
275	339	903	3.016	0.448	1.38 ± 0.03	1.58 ± 0.03
283	250	885	2.942	0.531	1.37 ± 0.07	1.58 ± 0.09
298	210	874	2.937	0.587	1.37 ± 0.05	1.58 ± 0.09
336	150	852	2.972	0.691	1.46 ± 0.04	1.59 ± 0.08
361	100	832	2.988	0.783	1.68 ± 0.03	1.63 ± 0.09
393	50	810	3.024	0.887	1.98 ± 0.06	1.50 ± 0.11

* density in $kg \cdot m^{-3}$; box length in nm; D in $10^{-9}\ m^2 \cdot s^{-1}$.

x_m lower than 0.5, methanol was treated as a solute in the solvent water; at higher mole fractions ($x_m > 0.5$) water was a solute in the solvent methanol. After energy minimisation, the systems were equilibrated for 25,000 timesteps. MD simulations of multiples of 5,000 timesteps were performed, resulting in 495,000 timesteps. During the simulation every 5 timesteps a new time origin was taken and the multiple particle autocorrelation function $\sum v_1^i(0) \cdot \sum v_1^j(t)$ was calculated. The Maxwell-Stefan diffusion coefficients were determined by using Eq. (6) for integration times of 1,000 and 1,500 timesteps (2 and 3 ps), resulting in 800 and 700 time origins used per run of 5,000 timesteps. Simultaneously, every 1,000 timesteps a new time origin was taken to calculate the velocity autocorrelation functions $vacf_i(t) \equiv \langle v_i(0) \cdot v_i(t) \rangle$ ($i = 1, 2$), resulting in 5 $vacf_i$ sets ($i = 1, 2$) per run of 5,000 timesteps. The self-diffusion coefficients of methanol and water were determined by using Eq. (7), and integrating over 1,000 timesteps (2 ps). The accuracy of the diffusion coefficients was estimated from the standard deviation of the block averages, into which the simulation data were grouped (at least 5 blocks).

5.1. Self-diffusion Coefficients

The self-diffusion coefficients were calculated by averaging over 495,000 simulation steps (495 $vacf_i$ sets) as well as by averaging over 395,000 simulation steps (395 $vacf_i$ sets), using the first 100,000 steps for further equilibration of the system. There was no significant difference between the values of the calculated self-diffusion coefficients. Results of the calculation over 495 $vacf_i$ sets are given in Table IV. In Figures 1 and 2 the calculated self-diffusion coefficients (300 K) are compared with values at 25°C, obtained

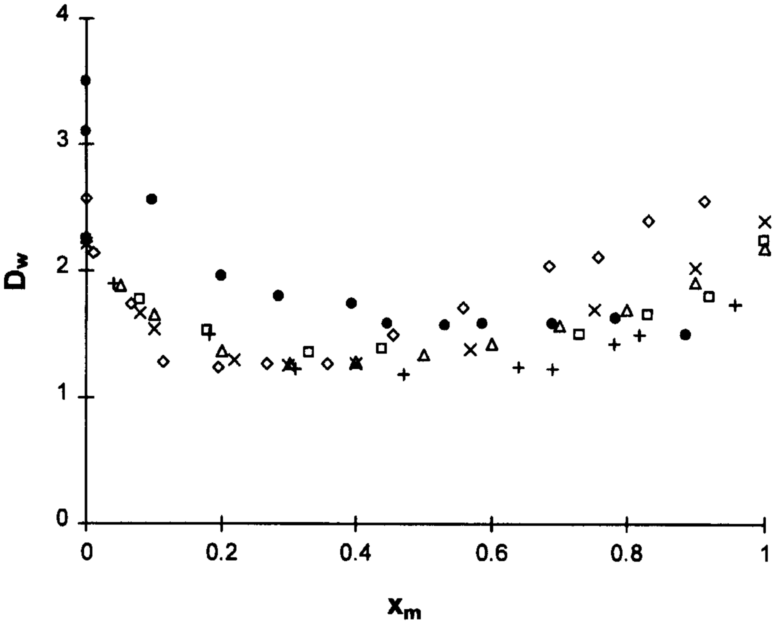

FIGURE 1 Self-diffusion coefficient of water (10^{-9} $m^2 \cdot s^{-1}$) as a function of the mole fraction methanol x_m: •, calculated in the simulation at 300 K; □, Kida and Uedaira [27], as estimated from the graph published; ×, Hertz and Leiter [28], as estimated from the graph published; Δ, Derlacki *et al.* [29]; +, Reimschüssel and Hawlicka [30]; ◇, Erdy-Grúz *et al.* [31].

from the literature. The self-diffusion coefficients of water and methanol, as given by Kida and Uedaira [27], were measured at 32°C. To compare these values with the other values from the literature, the self-diffusion coefficients of water were multiplied by a factor $2.299 \cdot 10^{-9}/2.733 \cdot 10^{-9}$ (equal to $D_{\text{water},25^\circ C}/D_{\text{water},32^\circ C}$), and the self-diffusion coefficients of methanol were multiplied by $2.50 \cdot 10^{-9}/2.75 \cdot 10^{-9}$ (equal to $D_{\text{methanol},\,25^\circ C}/D_{\text{methanol},32^\circ C}$).

Figure 1 shows a better agreement of the calculated self-diffusion coefficients of water with the literature values at high mole fractions of methanol; at low mole fractions of methanol the self-diffusion coefficient of water was high. The calculated self-diffusion coefficient of methanol agrees very well at high mole fractions of methanol, as shown in Figure 2; at low mole fractions the self-diffusion coefficient of methanol is high, too. The larger deviations of the self-diffusion coefficients at low values of the mole fraction methanol might be explained by the use of the force fields chosen. The SPC/E force field of water gives a much higher value of the

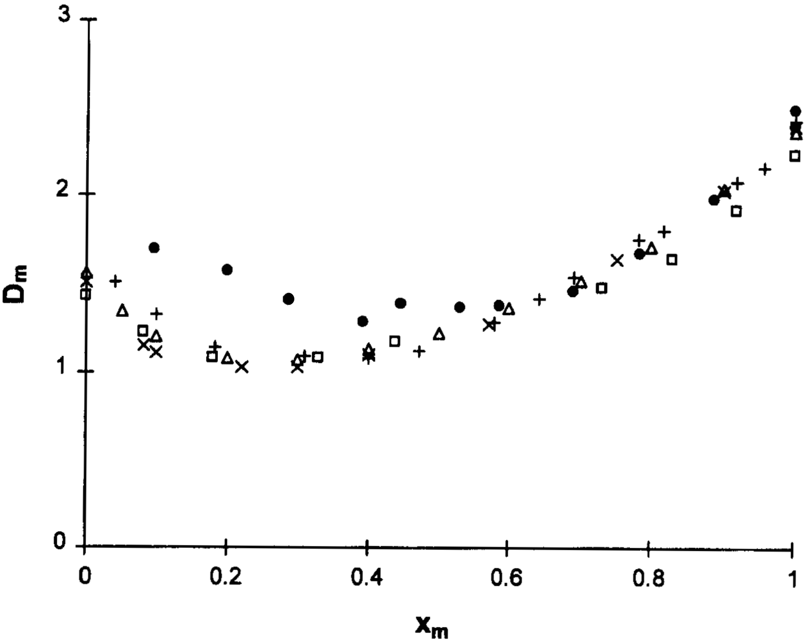

FIGURE 2 Self-diffusion coefficient of methanol ($10^{-9}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$) as a function of the mole fraction methanol x_m: •, calculated in the simulation at 300 K; □, Kida and Uedaira [27], as estimated from the graph published; ×, Hertz and Leiter [28], as estimated from the graph published; Δ, Derlacki *et al.* [29]; +, Reimschüssel and Hawlicka [30].

self-diffusion coefficient in pure water; the Van Leeuwen/Smit force field of methanol calculates the self-diffusion coefficient of methanol more accurate. At low mole fractions of methanol the influence of the SPC/E force field on the calculation of the diffusion coefficients might be larger, and the accuracy of the calculations might be smaller.

5.2. Mutual Diffusion Coefficients

The mutual Maxwell-Stefan diffusion coefficients D_{12} were determined by using Eq. (6) for the time origins obtained in a simulation of 495,000 timesteps as well for the time origins obtained in a simulation of 395,000 timesteps, using the first 100,000 steps for further equilibration of the system. The integration times were 1,000 and 1,500 timesteps (2 and 3 ps), and D_{12} was calculated for the methanol particles ($D_{12,m}$) as well as for the water particles ($D_{12,w}$). Results are listed in Table V. The difference between

TABLE V Maxwell-Stefan diffusion coefficients in methanol + water mixtures, calculated with Eq. (6)

$x_{methanol}$	$D^{*}_{12,m,495,2}$	$D^{*}_{12,m,495,2}$	$D^{*}_{12,m,395,2}$	$D^{*}_{12,m,395,2}$
0.097	2.2 ± 0.4	2.2 ± 0.4	1.8 ± 0.2	1.8 ± 0.2
0.201	2.0 ± 0.5	2.0 ± 0.4	1.7 ± 0.3	1.7 ± 0.2
0.286	1.9 ± 0.2	1.9 ± 0.2	1.7 ± 0.1	1.7 ± 0.1
0.394	2.1 ± 0.3	2.1 ± 0.3	1.8 ± 0.2	1.8 ± 0.2
0.448	1.8 ± 0.3	1.7 ± 0.3	1.5 ± 0.1	1.4 ± 0.1
0.531	2.3 ± 0.6	2.2 ± 0.6	1.7 ± 0.1	1.7 ± 0.1
0.587	2.2 ± 0.4	2.1 ± 0.4	1.9 ± 0.2	1.8 ± 0.2
0.691	2.9 ± 0.5	2.9 ± 0.5	2.5 ± 0.4	2.4 ± 0.3
0.783	2.7 ± 0.6	2.6 ± 0.6	2.2 ± 0.4	2.1 ± 0.4
0.887	3.5 ± 1.5	3.2 ± 1.5	2.1 ± 0.2	1.7 ± 0.2
0.097	2.4 ± 0.4	2.4 ± 0.4	2.0 ± 0.2	2.1 ± 0.3
0.201	1.5 ± 0.2	1.5 ± 0.1	1.5 ± 0.1	1.6 ± 0.1
0.286	1.8 ± 0.4	1.8 ± 0.3	1.6 ± 0.2	1.5 ± 0.2
0.394	1.8 ± 0.4	1.8 ± 0.4	1.5 ± 0.3	1.5 ± 0.3
0.448	1.8 ± 0.2	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1
0.531	1.9 ± 0.5	1.7 ± 0.4	1.4 ± 0.2	1.4 ± 0.1
0.587	1.8 ± 0.2	1.7 ± 0.1	1.7 ± 0.1	1.6 ± 0.1
0.691	2.7 ± 0.7	2.5 ± 0.6	2.2 ± 0.6	2.0 ± 0.5
0.783	2.3 ± 0.4	2.1 ± 0.3	2.0 ± 0.2	1.8 ± 0.2
0.887	3.1 ± 1.4	2.6 ± 1.3	1.8 ± 0.2	1.3 ± 0.2

*D in 10^{-9} $m^2 \cdot s^{-1}$; $D_{12,m,495,2}$: calculated with Eq. (6) for methanol, averaged over 495,000 steps, and integrated over 2 ps.

the values of $D_{12,m}$ and $D_{12,w}$ can be a measure for the accuracy of the simulation. In general, results were more accurate if the equilibration of the systems was increased with 100,000 timesteps. Figure 3 shows that an integration time of 2 ps was not always sufficient for the diffusion coefficient to become constant. The fluctuations in the calculated diffusion coefficients for long integration times will decrease, and the accuracy will increase, with an increasing number of time origins or simulation steps. For comparison with the literature values we used the average values of $D_{12,m}$ and $D_{12,w}$ obtained after further equilibration and by integrating over 3 ps. Since the diffusion coefficients given in the literature were Fick diffusion coefficients, they were divided by the thermodynamic factor Γ to obtain the Maxwell-Stefan diffusion coefficients (Eq. (4)). The values of Γ used were given by Mills *et al.* [33].

The simulated diffusion coefficients agreed fairly well with the literature values, as shown in Figure 4. The deviations were mainly caused by the short integration times of the multiple particle autocorrelation functions and the low number of simulation steps, resulting in a low number of time origins (Fig. 3).

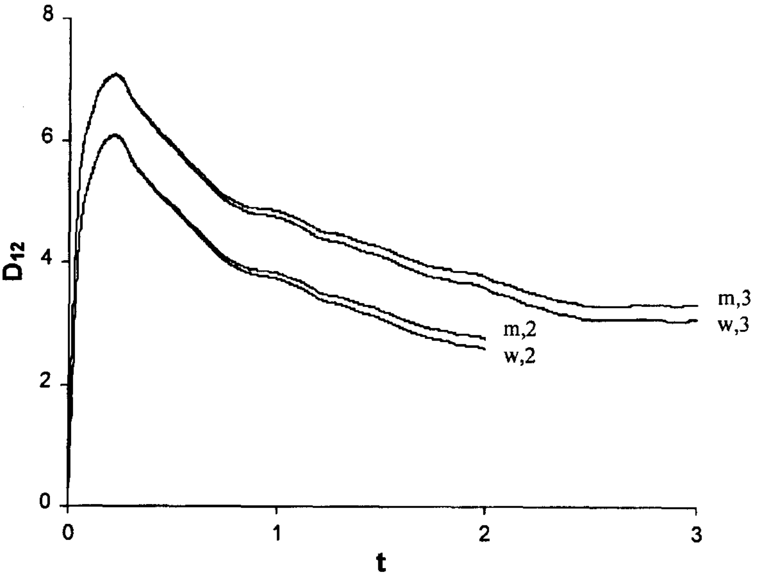

FIGURE 3 Maxwell-Stefan diffusion coefficient ($10^{-9}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$) as a function of the integration time t (ps): – m, 2, Eq. (6) for the methanol particles, integration time is 2 ps; – w, 2, Eq. (6) for the water particles, integration time is 2 ps; – m, 3, Eq. (6) for the methanol particles, integration time is 3 ps; – w, 3, Eq. (6) for the water particles, integration time is 3 ps.

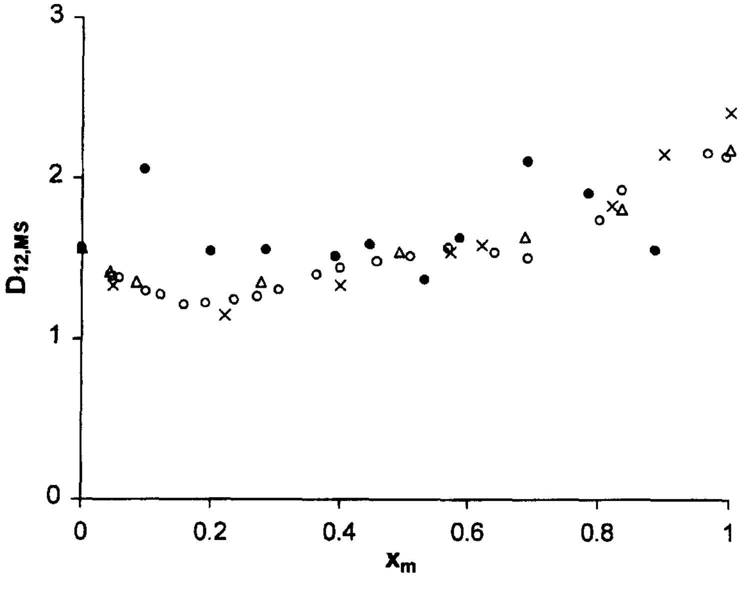

FIGURE 4 Mutual Maxwell-Stefan diffusion coefficient ($10^{-9}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$) as a function of the mole fraction methanol x_m: •, calculated in the simulation at 300 K; o, Van de Ven-Lucassen *et al.* [32]; ×, Hertz and Leiter [28], as estimated from the graph published; Δ, Derlacki *et al.* [29].

6. CONCLUSIONS

The self-diffusion and mutual Maxwell-Stefan diffusion coefficients in a binary system can be determined by the Green-Kubo method. The accuracy of the method is dependent on the parameters of the force field used in the molecular dynamics simulation. The force field of the methanol particles gives better results in the calculation of the self-diffusion coefficient of pure methanol than the force field of the water particles in the calculation of the pure water self-diffusion coefficient. In mixtures of water and methanol the self-diffusion coefficients of methanol and water are more accurate at high mole fractions of methanol, which can be explained by the greater influence of the methanol force field. The results of the simulation of the mutual Maxwell-Stefan diffusion coefficients agree fairly well with the experimental values, given in the literature. More accurate results can be obtained by using optimised parameters in the water force field, and by enlarging the system size, the integration time or the number of time origins, c.q. the duration of the MD runs.

APPENDIX

The GROMOS Force Field

The Gromos force field or interaction function has the following form

$$V^{\text{phys}}(\boldsymbol{r}; s) = V^{\text{bon}}(\boldsymbol{r}; s) + V^{\text{nonb}}(\boldsymbol{r}; s), \tag{A.1}$$

in which the term V^{bon} describes the interaction between covalently bonded atoms and V^{nonb} the non-bonded (van der Waals and electrostatic) interaction. The interaction between covalently bonded atoms is described by four terms: a bond-stretching term, a bond-angle term, a (harmonic) improper dihedral-angle bending term, and a (trigonometric) dihedral-angle torsion term. The bonded interaction is described by

$$\begin{aligned} V^{\text{nonb}}(\boldsymbol{r}; s) = {} & \sum_{\substack{\text{nonbonded} \\ \text{pairs}(i,j)}} \left[\frac{C_{12}(i, j)}{(r_{ij}^{4D})^6} - C_6(i, j) \right] \frac{1}{(r_{ij}^{4D})^6} \\ & + \sum_{\substack{\text{nonbonded} \\ \text{pairs}(i,j)}} \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_1} \left[\frac{1}{r_{ij}^{4D}} - \frac{(1/2)C_{rf}(r_{ij}^{3D})^2}{R_{rf}^3} - \frac{1 - (1/2)C_{rf}}{R_{rf}} \right] \end{aligned} \tag{A.2}$$

The first term in Eq. (A.2) represents the non-bonded van der Waals interaction. The Gromos van der Waals parameters for an atom pair (i,j) are derived from single atom van der Waals parameters using the relations

$$C_6(i,j) = C_6^{1/2}(i,i) \cdot C_6^{1/2}(j,j) \tag{A.3}$$

and

$$C_{12}(i,j) = C_{12}^{1/2}(i,i) \cdot C_{12}^{1/2}(j,j). \tag{A.4}$$

C_6 and C_{12} are a function of the Lennard-Jones energy- and size parameters.

The second term in Eq. (A.2) represents the electrostatic interaction. R_{rf} is the cut-off radius of the reaction field force. The reaction field force coefficient C_{rf} depends on the relative dielectric permittivity and an inverse Debye screening length.

The values of all parameters can be found in the interaction function parameter files of the GROMOS package.

An extensive description of the GROMOS force field is given in [13].

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