PFG-NMR and MD Simulation Study of Self-Diffusion Coefficients of Binary and Ternary Mixtures Containing Cyclohexane, Ethanol, Acetone and Toluene

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Abstract

Recently, Guevara-Carrion *et al.* published a comprehensive molecular dynamics (MD) study on the thermodynamic properties of binary mixtures containing methanol, ethanol, acetone, benzene, cyclohexane, toluene, and carbon tetrachloride which also includes results on self-diffusion coefficients. However, for the mixtures acetone/cyclohexane, acetone/ethanol, acetone/toluene, cyclohexane/ethanol, and toluene/ethanol, no experimental data on self-diffusion coefficients were available for comparison. Therefore, in the present work, self-diffusion coefficients in these mixtures were measured by ^1H NMR spectroscopy using pulsed field gradients (PFGs) at 298.15 K and ambient pressure. The experimental data were compared to the simulations of Guevara-Carrion *et al.* Good agreement was observed for all mixtures that do not contain ethanol, whereas, for ethanol-containing mixtures, the deviations were larger. This finding is attributed to deficiencies of the molecular model in describing the hydrogen-bonding of ethanol. Furthermore, self-diffusion data for the ternary mixture acetone/toluene/cyclohexane were

measured and compared to molecular simulation data from the present work. Good agreement was observed.

Introduction

Self-diffusion describes the movement of a molecule due to Brownian motion and is quantified by the self-diffusion coefficient.¹⁻³ The self-diffusion is influenced by the properties of the studied molecule and its interactions with the environment. Measurements of the self-diffusion coefficient, hence, provide insight into these interactions, the molecule’s environment, and its aggregation behavior.⁴⁻⁸

Self-diffusion coefficients in mixtures are closely related to the mutual diffusion coefficients, that are needed for describing mass transfer.⁹ At infinite dilution, the self-diffusion coefficient of the infinitely diluted component in a mixture is identical with the mutual diffusion coefficient. Simultaneously, the self-diffusion coefficients of the other components are not connected to the mutual diffusion coefficient at this composition. For the general case, there is no analytical formula that would relate the self-diffusion and the mutual diffusion coefficients in a mixture, but it is obvious that both properties are closely connected on the molecular scale. Both can be obtained from molecular simulation, and a molecular model that describes self-diffusion may be expected to also describe mutual diffusion well.

Hence, there are many good reasons why self-diffusion coefficients are valuable benchmarks for testing molecular models,¹⁰⁻¹² especially as they can be obtained from molecular simulations simply by monitoring the mean-squared displacement.¹³

Several methods for predicting self-diffusion coefficients have been described in the literature,^{14,15} but they are usually limited to pure components or mixtures in which the diffusing component is infinitely diluted. Furthermore, their accuracy is often not satisfactory, especially for liquid mixtures. This is particularly troublesome, as experimental data on self-diffusion coefficients in mixtures are comparatively rare, at least for cases other than

infinite dilution.

For the experimental determination of self-diffusion coefficients, only few methods are available: tracer measurements,¹⁶ neutron scattering,¹⁷ and nuclear magnetic resonance with pulsed field gradients (PFG-NMR).¹⁸

Tracer measurements use radioactive isotopes in order to track the diffusive motion. However, the diffusive motion is generally influenced by isotopic effects.^{19,20} The inelastic neutron scattering method does not suffer from this problem. However, the models for interpreting the results from this method are complicated and the measurements are tedious.

PFG-NMR spectroscopy overcomes these disadvantages, as it labels individual molecules without perturbing the system. The labeling is achieved by using a magnetic field gradient pulse to encode the position of each measured molecule in the sample. This encoding is accomplished by altering the precession phase of nuclear spins in a defined way. Upon movement of the molecules, the phase spread is not fully reversed by the following decoding gradient pulse and the intensity of the acquired signal is reduced.²¹ The measured difference is directly related to the self-diffusion coefficients of the labeled molecules.

In 2016, Guevara-Carrion *et al.*²² published a molecular dynamics study of various thermodynamic properties of methanol, ethanol, acetone, benzene, cyclohexane, toluene, and carbon tetrachloride and all of their binary mixtures. Self-diffusion coefficients obtained through MD simulations of the pure liquids and the mixtures were compared to available experimental data as well as to results from the predictive equations of Li *et al.*²³ and Liu *et al.*²⁴ For five of the possible mixtures (acetone/cyclohexane, acetone/ethanol, acetone/toluene, cyclohexane/ethanol, and toluene/ethanol), no experimental data were available. In this paper, the self-diffusion coefficients of these five mixtures were investigated by ¹H PFG-NMR spectroscopy at 298.15 K and ambient pressure. The data were compared to the simulation data of Guevara-Carrion *et al.*²² as well as the predictive equations of Li *et al.*²³ and Liu *et al.*²⁴ Furthermore, the ternary mixture acetone/toluene/cyclohexane was investigated by ¹H PFG-NMR spectroscopy and MD simulations.

Several studies of self-diffusion in other binary and ternary mixtures with at least one component being acetone,^{25,26} cyclohexane,^{26–34} toluene^{27,34–36} or ethanol^{25,37–40} have been published in the literature.

Experimental Procedure

¹H PFG-NMR measurements were carried out with a NMR spectrometer with a superconducting magnet of a magnetic field strength of 9.4 T corresponding to a proton Larmor frequency of 400.25 MHz. The NMR spectrometer is equipped with a probe with cryogenically cooled electronics (magnet Ascend 400, console Avance III HD 400, probe CyroProbe Prodigy, Bruker Biospin, Germany). The spectrometer’s temperature sensor was calibrated with a platinum resistance thermometer (Pt-100) that was, in turn, calibrated in our laboratory using a certified standard. The standard uncertainty of the temperature measurement is estimated as $u(T) = 0.1$ K. Special sample tubes with an outer diameter of 2.5 mm (Deutero GmbH, Germany) were used in order to minimize sample convection⁴¹ and radiation damping.⁴²

A stimulated spin-echo technique with bipolar pulsed gradients⁴³ was applied as implemented in the NMR spectrometer’s software (pulse sequence: `stebpgp1s`). The self-diffusion coefficient of species i (D_i) is obtained from a fit of the natural logarithm of the relative NMR signal intensity against the squared gradient strength according to Equation (1).²¹

$$\ln \left(\frac{I}{I_0} \right) = -D_i \gamma^2 \delta^2 \left(\Delta - \frac{1}{3} \delta \right) g^2 \quad (1)$$

where I is the signal intensity, I_0 is the signal intensity without a gradient, γ is the gyromagnetic ratio, δ is the duration of the gradient pulse, Δ is the diffusion time (i.e. the time between the midpoints of the gradient pulses), and g is the gradient strength.

A systematic error of diffusion measurements is the spatial nonuniformity of the applied field gradient.⁴⁴ The spatial gradient profile of the used probe head was checked with a

spatially resolved PFG-NMR measurement and weak nonlinearity in the gradient profile was observed. To a certain degree, this may be compensated by fitting a calibration constant to experimental data of a substance with a precisely known diffusion coefficient such as water.⁴⁵ Depending on the hardware, this can already largely alleviate the error. Furthermore, a more thorough correction is achieved by employing a polynomial expression for Equation (1) as demonstrated by Connell *et al.*⁴⁶ In the present work, a second-order polynomial was used for this correction. Additionally, a compensation term for the used bipolar gradients is included, resulting in Equation (2).

$$\ln\left(\frac{I}{I_0}\right) = -\sum_{n=1}^2 c_n \left(D_i \gamma^2 \delta^2 \left(\Delta - \frac{\delta}{3} - \frac{\tau}{2} \right) g^2 \right)^n \quad (2)$$

In Equation (2), the c_n values (in this case, c_1 and c_2) are probe-specific fit coefficients and τ is the correction constant due to the usage of bipolar gradients. The sum of the squared relative errors between the experimental data and Equation (2) was employed as an objective function.

The diffusion time Δ was chosen as 50 ms for all measurements and the gradient strength g was incremented following a square root relationship from 2.5 to 48.5 G cm⁻¹. Each diffusion experiment consisted of 16 gradient steps with 16 scans, respectively, with a prescan delay that was chosen long enough to ensure complete magnetization relaxation. The gradient pulse duration δ was adjusted to the respective sample (between 0.6 and 4 ms). The time constant τ was chosen as 0.2 ms, corresponding to the time delay between the bipolar gradient lobes. Automatic baseline and phase correction of the spectra were performed with the processing tool developed by Sawall *et al.*⁴⁷

Chemicals

Table 1 gives an overview of the chemicals that were used in the present work, their suppliers, and their purity. The samples were prepared gravimetrically using a laboratory balance (Mettler-Toledo AG204) with an accuracy of ± 0.0001 g according to the calibration protocol. The total mass of each sample that was prepared was approximately 10 g, from which the required NMR sample amount was taken. The resulting expanded uncertainty in the mole fraction of the samples is $U = 0.001 \text{ mol}\cdot\text{mol}^{-1}$ ($k = 2$).

Table 1: Overview of chemicals that were used with the respective suppliers and purities.

IUPAC name	Acetone (Propan-2-one)	Ethanol (Ethanol)	Toluene (Methylbenzene)	Cyclohexane (Cyclohexane)

Molar mass/ $\text{g}\cdot\text{mol}^{-1}$	58.08	46.07	92.14	84.16
Supplier	Merck KGaA (Darmstadt, Germany)			Fisher Chemical (Loughborough, U.K.)
Purity/ $\text{mol}\cdot\text{mol}^{-1}$	≥ 0.999 (Uvasol®)			≥ 0.9998

Semiempirical Methods for Predicting the Self-Diffusion Coefficient

Li *et al.*²³ extended the equation of Carman and Stein⁴⁸ by taking into account cluster formation:

$$D_i = D_i^0 \frac{\eta_i}{\eta} \left(\frac{n_i^0}{1 + (n_i^0 - 1)x_i} \right)^{0.5} \quad (3)$$

D_i is the self-diffusion coefficient of substance i in a binary mixture at a given mole

fraction x_i . D_i^0 is the self-diffusion coefficient of the pure substance, η_i and η_j are the shear viscosities of the pure substances and η is the shear viscosity of the mixture. n_i^0 is the degree of association, defined as

$$n_i^0 = \frac{\eta_j D_i^{x_j \rightarrow 1}}{(\eta_i D_i^0)^2}. \quad (4)$$

Here $D_i^{x_j \rightarrow 1}$ represents the self-diffusion coefficient of component i at infinite dilution in component j which is identical to the mutual diffusion coefficient at infinite dilution.

Based on kinetic theory,^{49,50} McCarty and Mason⁵¹ and Miller and Carman⁵² derived an equation for predicting the self-diffusion coefficient in binary gas mixtures. Assuming a constant mutual diffusion coefficient in the mixture, this equation reduces to Equation 5. Liu *et al.*²⁴ proposed its use for weakly nonideal, multicomponent liquids:

$$D_i = \frac{1}{\sum_j \frac{x_j}{D_i^{x_j \rightarrow 1}}}. \quad (5)$$

The sum ranges over all components in the mixture.

In this work, the methods by Li *et al.*²³ and Liu *et al.*²⁴ are employed by using the measured self-diffusion coefficients of the pure substances D_i^0 as input. Values for the self-diffusion coefficients at infinite dilution $D_i^{x_j \rightarrow 1}$ are generated through extrapolation of the experimental self-diffusion data from this work toward infinite dilution. Viscosity data for Equation (3) (Li *et al.*²³) were obtained from the literature for the mixtures toluene/cyclohexane,²⁷ acetone/cyclohexane,⁵³ acetone/ethanol,⁵³ acetone/toluene,⁵⁴ cyclohexane/ethanol⁵³ and toluene/ethanol.⁵⁵ For the mixture toluene/ethanol, the available data were linearly extrapolated to 298.15 K.

Molecular Simulation

Rigid multicenter Lennard-Jones (LJ) models with superimposed point quadrupoles and point dipoles were used for acetone,⁵⁶ toluene²² and cyclohexane¹⁰ in molecular dynamics simulations. The interactions between LJ sites of different molecules were determined by the Lorentz-Berthelot combining rules, and no adjustable parameters were employed. Thus, the presented simulations are predictions from pure component data. The molecular model files were used as provided by the MolMod database⁵⁷ (database IDs: acetone 139, cyclohexane 156, toluene 162).

The simulations were carried out with the simulation package *ms2*⁵⁸ (version 3.0.0). In a first step, the density was calculated in the isobaric-isothermal ensemble (NpT) for 298.15 K and 0.1 MPa. This was accomplished using 1.2×10^5 equilibration steps and 5×10^5 production steps. The obtained density was then used in a canonical ensemble (NVT) simulation at the same temperature and composition. Here, 3×10^5 equilibration steps and 10^7 production steps were utilized in order to sample the velocity autocorrelation function. The time step length was 0.877 fs. The self-diffusion coefficients of all components in the mixture were calculated with the Green-Kubo formalism:^{13,59–62}

$$D_i = \frac{1}{3N_i} \int_0^\infty \left\langle \sum_{k=1}^{N_i} \mathbf{v}_{i,k}(0) \cdot \mathbf{v}_{i,k}(t) \right\rangle dt \quad (6)$$

where N_i is the number of molecules of species i and the bracketed term is the ensemble average of the velocity autocorrelation function with $\mathbf{v}_{i,k}(t)$ as the velocity vector of molecule k at a time t .

The equations of motion were integrated with a fifth-order Gear predictor-corrector numerical integrator. Velocity scaling and Anderson’s barostat were used to maintain constant temperature and pressure. The integration time step was 0.877 fs and the sampling length of the autocorrelation functions, which are used to calculate the self-diffusion coefficient, was 17.5 ps. The system size was 4000 molecules. The cutoff radius for the explicit calculation

of intermolecular interactions was 17.5 Å. For corrections to the LJ interactions at long ranges, angle-averaging by Lustig⁶³ was applied. Electrostatic long-range interactions were accounted for by the reaction field method with conducting boundary conditions. Statistical uncertainties were estimated with a block averaging method.⁶⁴

Results and Discussion

Binary Mixtures

The self-diffusion coefficients of the pure liquids measured in the present work are compared to literature data in Figure 1, in order to check the accuracy of the present diffusion measurements. Most of the literature values were taken from a review paper by Suárez-Iglesias *et al.*,⁶⁵ but the original sources are indicated as short references. For this comparison, only literature sources were considered which stated a measurement temperature of 298.15 K $\pm$ 0.2 K. The original sources and corresponding experimental temperatures and self-diffusion coefficients are summarized in Table A.1 in the Appendix. Figure 1 shows that, for all four studied substances, the experimental data from the present work lie almost central in the band of trustworthy data from the literature. The relative standard uncertainty of the determination of D_i from the fit to the experimental NMR data using Equation (2) was $u_r(D_i) = 0.01$. The statistical relative standard uncertainty estimated from the results of repeated measurements of selected systems also was $u_r(D_i) = 0.01$. Therefore, an expanded relative uncertainty of $u_r(D_i) = 0.02$ ($k = 2$) is assumed for the experimental data. This uncertainty estimation is also valid for the experimental data of the binary and ternary mixtures that are presented in this paper.

As a rule of thumb, an inverse relationship between the self-diffusion coefficient and the molecular mass is expected. This relationship would result in an increase of the self-diffusion coefficient in the order: toluene, cyclohexane, acetone, ethanol. The actual sequence is: ethanol, cyclohexane, toluene, acetone. The observed order can be explained by taking into

Figure 1: Comparison of literature data (open circles with error bars where available) and experimental data (red) from this work for self-diffusion coefficients of acetone^{26,66–75}, toluene,^{32,34–36,76–79} cyclohexane^{19,26,29–32,34,38,45,66,70,75,77,80–90}, and ethanol^{25,70,74,75,85,89–99} at ambient pressure. The measurement temperatures lie between 297.99 and 298.32 K and are given for each reference in Table A.1. Where a reference is mentioned more than once, different methods were used.

account the specific nature of the considered molecules. For ethanol, this is the association of molecules due to hydrogen-bonding.³⁷ In the case of cyclohexane, the chair/twist boat conformational equilibrium¹⁰⁰ offers additional degrees of freedom. Both effects lead to a lowering of molecular mobility and consequentially a lowering of the self-diffusion coefficient.

Figure 2 shows the measured self-diffusion coefficients of the six binary mixtures that can be obtained from toluene, acetone, cyclohexane, and ethanol. Each diagram depicts the self-diffusion coefficients of each component in the mixtures as a function of the composition. The experimental data from the present work are compared to the predictions from molecular simulation by Guevara-Carrion *et al.*²² as well as to results from the methods of Li *et al.*²³ and Liu *et al.*²⁴ The numerical experimental data from this work are given in Table 2.

In Figure 2, also experimental data from the literature is included, where such data is available. This is only the case for the system cyclohexane/toluene, which has been studied by Merzliak *et al.*³³ using PFG-NMR. Merzliak *et al.*³³ reported self-diffusion coefficients from multiple measurements for a single mole fraction. From these values, the arithmetic mean was calculated. The uncertainties of the measurements are included in Figure 2 as reported by Merzliak *et al.*³³

In all studied systems, the component that shows the higher self diffusion coefficient as a pure substance, also has a higher self diffusion coefficient in the mixture. As the mole fraction of this component increases, the self-diffusion coefficients of both constituents gradually increase.

For all mixtures that do not contain ethanol the distance between the two self-diffusion coefficients does not depend strongly on the concentration. In contrast, for all mixtures that contain ethanol, it is found that, as the ethanol concentration decreases, the self-diffusion coefficient of ethanol increases more strongly than that of the other component. In the mixture toluene/ethanol, this even results in an intersection of the curves of both self-diffusion coefficients, cf. Figure 2. This is explained by the fact that the hydrogen-bonding of ethanol becomes less prevalent at low ethanol concentrations such that the mobility increases.

Figure 2: Comparison of experimental self-diffusion coefficients of the binary mixtures measured in the present work, the MD simulation results of Guevara-Carrion *et al.*²² and the values obtained using the methods of Li *et al.*²³ (Equations (3)) and Liu *et al.*²⁴ (Equation (5)). The data points obtained through the latter two methods were connected by straight lines. All results are for 298.15 K and ambient pressure. Additionally, for the mixture toluene/cyclohexane, the experimental data of Merzliak *et al.*³³ are shown. The error bars for the own experimental results are within the symbol size.

Table 2: Experimental data for the self-diffusion coefficients in the binary mixtures of acetone, toluene, cyclohexane, and ethanol at 298.15 K and ambient pressure.

Toluene/Cyclohexane			Cyclohexane/Ethanol			Acetone/Toluene		
x_1	D_1	D_2	x_1	D_1	D_2	x_1	D_1	D_2
mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹		mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹		mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹	
0.00		1.441	0.00		1.069	0.00		2.276
0.05	1.801	1.519	0.05	1.582	1.100	0.05	2.972	2.325
0.10	1.861	1.594	0.10	1.589	1.083	0.10	3.008	2.372
0.20	1.982	1.736	0.20	1.620	1.078	0.20	3.135	2.494
0.30	2.076	1.861	0.30	1.636	1.065	0.30	3.268	2.604
0.40	2.154	1.968	0.40	1.630	1.046	0.40	3.356	2.696
0.50	2.212	2.056	0.50	1.622	1.030	0.50	3.503	2.831
0.60	2.257	2.128	0.60	1.631	1.041	0.60	3.668	2.977
0.70	2.275	2.175	0.70	1.613	1.046	0.70	3.855	3.152
0.80	2.281	2.215	0.80	1.560	1.054	0.80	4.050	3.337
0.90	2.293	2.252	0.90	1.518	1.149	0.90	4.271	3.540
0.95	2.286	2.251	0.95	1.484	1.296	0.95	4.390	3.681
1.00	2.276		1.00	1.441		1.00	4.552	

Toluene/Ethanol			Acetone/Ethanol			Acetone/Cyclohexane		
x_1	D_1	D_2	x_1	D_1	D_2	x_1	D_1	D_2
mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹		mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹		mol·mol ⁻¹	10 ⁻⁹ ·m ² ·s ⁻¹	
0.00		1.069	0.00		1.069	0.00		1.441
0.05	1.739	1.105	0.05	2.086	1.209	0.05	2.318	1.561
0.10	1.798	1.141	0.10	2.231	1.341	0.10	2.412	1.681
0.20	1.908	1.212	0.20	2.578	1.635	0.20	2.620	1.898
0.30	2.002	1.288	0.30	2.890	1.922	0.30	2.895	2.127
0.40	2.074	1.363	0.40	3.174	2.230	0.40	3.115	2.321
0.50	2.139	1.444	0.50	3.445	2.538	0.50	3.317	2.499
0.60	2.190	1.545	0.60	3.706	2.855	0.60	3.557	2.725
0.70	2.251	1.669	0.70	3.937	3.170	0.70	3.860	3.019
0.80	2.286	1.839	0.80	4.149	3.506	0.80	4.051	3.229
0.90	2.308	2.171	0.90	4.319	3.898	0.90	4.314	3.534
0.95	2.333	2.592	0.95	4.430	4.005	0.95	4.373	3.653
1.00	2.276		1.00	4.552		1.00	4.552	

The index "1" represents the first-denoted substance, index "2" the second. Expanded uncertainty: $U(x) = 0.001 \text{ mol} \cdot \text{mol}^{-1}$ ($k = 2$). Expanded relative uncertainty: $u_r(D_i) = 0.02$ ($k = 2$). Standard uncertainty: $u(T) = 0.1 \text{ K}$.

The agreement between the experimental data from the present work and the predictions from the molecular simulations is excellent for the system acetone/toluene and good for the systems toluene/cyclohexane and acetone/cyclohexane. This is different for the systems that contain ethanol. For the system acetone/ethanol, the agreement is still fair, whereas the predictions for the systems cyclohexane/ethanol and toluene/ethanol are poor. This indicates that the effect of hydrogen-bonding on the self-diffusion is not well described by the molecular models. This effect is particularly important in mixtures of a hydrogen-bonding component like ethanol with a non-hydrogen-bonding component like cyclohexane or toluene¹⁰¹ and less important in mixtures in which both components show hydrogen-bonding (acetone serves as a hydrogen-bond acceptor).

The values predicted through the equation of Li *et al.*²³ are higher than those predicted by the equation of Liu *et al.*²⁴ The predicted values approach the experimental data at the edges of the mole fraction range per definition as the predictive equations use these values as input parameters. The results from the equation of Li *et al.*²³ are splines between points for which viscosity data were available. With the exception of the relatively simple case of acetone/toluene, the self-diffusion coefficients in all mixtures that were studied in the present work are only poorly predicted and strongly varying deviations are observed. With the exception of the most ideal systems, only a rough estimation is provided by these equations.

Ternary Mixture

The self-diffusion coefficients of all components in 22 ternary mixtures in the system acetone/cyclohexane/ toluene were measured in the present work at 298 K by ¹H PFG-NMR spectroscopy. The experimental studies were complemented by a MD simulation study in which, for the same state points, the self-diffusion coefficients were determined for each component as described above. The numerical results of both the experimental and the simulation study are reported in Table 3. Figure 3 shows a comparison of the data sets.

Table 3: Experimental data and MD simulation data for the self-diffusion coefficients in the ternary mixture of acetone(1)/cyclohexane(2)/toluene(3) at 298.15 K and ambient pressure.

		Exp.			Sim.		
x_1	x_2	D_1	D_2	D_3	D_1	D_2	D_3
mol·mol ⁻¹		10 ⁻⁹ ·m ² ·s ⁻¹			10 ⁻⁹ ·m ² ·s ⁻¹		
0.05	0.05	3.015	2.326	2.361	2.94 (1)	2.23 (1)	2.415 (4)
0.05	0.15	3.017	2.303	2.368	2.89 (1)	2.181 (6)	2.365 (4)
0.05	0.35	2.984	2.218	2.344	2.79 (1)	2.080 (5)	2.28 (5)
0.05	0.55	2.866	2.078	2.259	2.69 (1)	1.954 (4)	2.168 (5)
0.05	0.75	2.669	1.868	2.119	2.55 (1)	1.815 (4)	2.038 (5)
0.05	0.90	2.498	1.662	1.935	2.42 (1)	1.699 (3)	1.923 (9)
0.15	0.80	2.646	1.887	2.158	2.628 (8)	1.858 (4)	2.11 (1)
0.35	0.60	3.080	2.301	2.572	3.052 (6)	2.179 (4)	2.47 (1)
0.55	0.40	3.581	2.721	2.967	3.459 (6)	2.513 (6)	2.82 (1)
0.75	0.20	4.019	3.184	3.330	3.885 (7)	2.951 (7)	3.19 (1)
0.90	0.05	4.344	3.564	3.634	4.268 (7)	3.37 (2)	3.60 (2)
0.80	0.05	4.127	3.350	3.397	4.041 (7)	3.15 (1)	3.372 (9)
0.60	0.05	3.729	2.998	3.044	3.644 (6)	2.80 (1)	3.015 (7)
0.40	0.05	3.364	2.665	2.710	3.327 (6)	2.56 (1)	2.750 (6)
0.20	0.05	3.114	2.445	2.484	3.078 (7)	2.36 (1)	2.536 (5)
0.33	0.33	3.290	2.508	2.671	3.140 (7)	2.325 (5)	2.562 (6)
0.20	0.20	3.100	2.396	2.490	3.018 (8)	2.284 (6)	2.482 (5)
0.20	0.40	3.055	2.303	2.457	2.926 (8)	2.180 (5)	2.398 (5)
0.20	0.60	2.881	2.136	2.360	2.827 (7)	2.039 (4)	2.279 (6)
0.40	0.20	3.370	2.628	2.738	3.283 (6)	2.480 (7)	2.700 (6)
0.40	0.40	3.283	2.509	2.705	3.217 (7)	2.364 (5)	2.619 (7)
0.60	0.20	3.713	2.908	3.041	3.602 (6)	2.726 (7)	2.974 (8)

For the MD results, the self-diffusion coefficient for each component is given with the last digit uncertainty in parentheses. Expanded uncertainty: $U(x) = 0.001 \text{ mol} \cdot \text{mol}^{-1}$ ($k = 2$). Expanded relative uncertainty: $u_r(D_i) = 0.02$ ($k = 2$). Standard uncertainty: $u(T) = 0.1 \text{ K}$.

Figure 3: Comparison of experimental self-diffusion coefficient data (black dots connected by a colored surface) and MD simulation data (black dots connected by a gray surface) of the ternary mixture acetone/cyclohexane/toluene at 298.15 K and ambient pressure. The data of the binary systems are visible at the edges. The error bars are omitted for clarity.

The results for the three self-diffusion coefficients are shown as a function of the composition in individual diagrams. The experimental self-diffusion coefficients of the three components vary in a simple manner, and no intersections are observed. The maxima are reached in the acetone-rich corner and the minima in the cyclohexane-rich corner. The values in the corners define a plane that describes the data reasonably well but not perfectly. The small deviations from linearity are systematic. This holds for both the experimental results and the results from the MD simulations, which agree generally very well. The small deviations between the experimental data and the simulation data can mainly be attributed to the deviations of the prediction of the self-diffusion coefficients of the pure components and those at infinite dilution, that are found in the corners in the diagrams shown in Figure 3.

In most cases, the simulation slightly underestimates the self-diffusion coefficients. The largest relative deviation of 7.7 % is found for cyclohexane (at $x_{\text{Acetone}} = 0.55 \text{ mol}\cdot\text{mol}^{-1}$ and $x_{\text{Cyclohexane}} = 0.4 \text{ mol}\cdot\text{mol}^{-1}$). Overall, the relative deviations are relatively small, with averages of 3.2, 5.1, and 2.4 % for the self-diffusion coefficients of acetone, cyclohexane, and toluene, respectively.

As the method of Liu *et al.*²⁴ only gave poor results for the binary systems, it is not astonishing that it also gives poor results for the ternary system. The corresponding results are not shown here. The method of Li *et al.*²³ cannot even be applied, as it would require information on the viscosity in the ternary system, which is not available.

Conclusions

The self-diffusion coefficients of the binary mixtures comprising acetone, cyclohexane, toluene, and ethanol at 298.15 K were measured by PFG-NMR. A comparison with literature data for the pure components confirmed the reliability of the experimental method. The data for the binary systems are compared to the MD simulation data of Guevara-Carrion *et al.*²² and two methods for predicting self-diffusion coefficients in mixtures (Li *et al.*²³ and Liu *et*

*al.*²⁴). They give only poor results in most of the studied systems. In contrast, the MD simulations showed good results in all systems that do not contain ethanol. The deviations that were observed in the ethanol-containing systems are most likely related to problems of the molecular model of ethanol in describing the hydrogen-bonding of ethanol, which leads to the formation of aggregates and, hence, a lowering of the self-diffusion coefficient. Furthermore, the ternary mixture acetone/cyclohexane/toluene was investigated by both PFG-NMR and MD simulations. The MD simulations predict the simple behavior of the self-diffusion coefficients in this ternary system well. The study underpins that PFG-NMR is an accurate and fast method for measuring self-diffusion coefficients and yields also results for low concentrations, such that information on mutual diffusion can be obtained. It also shows that MD simulations are an interesting option for predicting self-diffusion coefficients of real binary and ternary mixtures. In the present study, they yielded distinctly better results than methods from the literature that were developed exclusively for that purpose.

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Appendix

Table A.1: Literature values of self-diffusion coefficients of acetone, cyclohexane, ethanol and toluene at ambient pressure. Given are the short reference which is also used in Figure 1, the reported temperature of the measurements, and the reported value of the self-diffusion coefficient. The values from this work are included. Where more than one value is given for the same reference, multiple methods have been used. When the reference presented more than one value obtained from the same method, the mean value was calculated.

Substance	Short reference	T/K	$10^9 \cdot D_i/\text{m}^2\cdot\text{s}^{-1}$	Ref.
Acetone	Zeidler (1965), Goldammer and Zeidler (1969)	298.16	5.2	66,67
	McCall and Douglass (1967)	298.16	4.86	26
	Krüger and Weiss (1970)	298.16	4.30	68
	O'Reilly and Peterson (1971)	298.00	4.00	69
	Claessens <i>et al.</i> (1984)	298.16	4.97	70
	LeBihan and Breton (1985)	298.16	4.16	71
	Le Bihan <i>et al.</i> (1986)	298.16	4.47	72
	Canet <i>et al.</i> (1989)	298.16	4.98	73
	Holz <i>et al.</i> (1996)	298.16	4.57	74
	Viel <i>et al.</i> (2008)	298.16	4.53	75
	This work	298.15	4.552	
Toluene	Kamal and McLaughlin (1968)	298.16	2.230	32
	O'Reilly and Peterson (1972)	297.99	2.130	76
	Ghai and Dullien (1974)	298.16	2.290	35
	Reimschüssel and Hawlicka (1977)	298.16	1.740	34
	Fischer and Weiss (1986)	298.16	2.376	77
	Pickup and Blum (1989)	298.16	2.660	36
	Harris <i>et al.</i> (1993)	298.14	2.21	78
		298.14	2.292	78
	Mischler <i>et al.</i> (1995)	298.16	2.346	79
		298.16	2.277	79
	This work	298.15	2.276	
Cyclohexane	Birkett and Lyons (1965)	298.16	1.42	80
	Kulkarni <i>et al.</i> (1965)	298.16	1.433	81
	Mills (1965)	298.16	1.475	31
	Zeidler (1965)	298.16	1.7	66
	Kamal and McLaughlin (1966. 1968)	298.16	1.41	32
	McCall and Douglass (1967)	298.16	1.42	26

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Table A.1 – *Continued from previous page*

Substance	Short reference	T/K	$10^9 \cdot D_i/\text{m}^2 \cdot \text{s}^{-1}$	Ref.
	Kessler <i>et al.</i> (1969)	298.16	1.46	30
	McCool and Woolf (1972)	298.20	1.450	82
	Mills (1975)	298.16	1.457	19
		298.16	1.463	19
	Reimschüssel and Hawlicka (1977)	298.16	1.464	34
	Freer and Sherwood (1980)	298.18	1.441	83
		298.18	1.450	83
		298.18	1.453	83
		298.18	1.463	83
	Hawlicka and Reimschüssel (1981)	298.20	1.464	29
	Claessens <i>et al.</i> (1984)	298.16	1.88	70
	Kato (1985)	298.16	1.47	84
	Fischer and Weiss (1986)	298.32	1.428	77
	Holz and Weingärtner (1991)	298.16	1.42	85
	Piton <i>et al.</i> (1993)	298.16	1.47	86
	Todica <i>et al.</i> (1994)	298.00	1.40	87
	Malveau <i>et al.</i> (1998)	298.16	1.51	88
	Holz <i>et al.</i> (2000)	298.16	1.424	45
	Tofts <i>et al.</i> (2000)	298.16	1.474	89
	Kato <i>et al.</i> (2006)	298.16	1.457	90
	Iwahashi and Kasahara (2007)	298.16	1.58	38
	Viel <i>et al.</i> (2008)	298.16	1.45	75
	This work	298.15	1.441	
Ethanol	Partington <i>et al.</i> (1952)	298.16	0.768	91
	Graupner and Winter (1952)	298.16	1.05	92
	Johnson and Babb (1956)	298.16	1.02	93
	Hardt (1959)	298.16	1	25
	Powles and Cuttler (1959)	298.16	1.954	94
	Rathbun and Babb (1961)	298.16	1.02	95
	Uminski <i>et al.</i> (1965)	298.16	1.04	96
	Rothschild (1970)	298.16	1.3	97
	Pratt and Wakeham (1977)	298.16	1.16	98
	Claessens <i>et al.</i> (1984)	298.16	1.12	70
	Hurle <i>et al.</i> (1985)	298.20	1.086	99
		298.20	1.075	99
	Holz and Weingärtner (1991)	298.16	1.07	85

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Table A.1 – *Continued from previous page*

Substance	Short reference	T/K	$10^9 \cdot D_i/\text{m}^2 \cdot \text{s}^{-1}$	Ref.
	Holz <i>et al.</i> (1996)	298.20	1.07	⁷⁴
	Tofts <i>et al.</i> (2000)	298.16	1.080	⁸⁹
	Kato <i>et al.</i> (2006)	298.16	1.07	⁹⁰
	Viel <i>et al.</i> (2008)	298.16	0.96	⁷⁵
	This work	298.15	1.069	

References

- (1) Einstein, A. Über die von der Molekularkinetischen Theorie der Wärme Geforderte Bewegung von in Ruhenden Flüssigkeiten Suspendierten Teilchen. *Ann. Phys.* **1905**, *322*, 549–560.
- (2) Tsimpanogiannis, I. N.; Moulton, O. A.; Franco, L. F. M.; Spera, M. B. d. M.; Erdős, M.; Economou, I. G. Self-Diffusion Coefficient of Bulk and Confined water: A Critical Review of Classical Molecular Simulation Studies. *Mol. Simul.* **2019**, *45*, 425–453.
- (3) Larsson, K.-E. Self-Diffusion in Simple Liquids. *J. Phys.: Condens. Matter* **1994**, *6*, 2835–2846.
- (4) Avram, L.; Cohen, Y. Diffusion NMR of Molecular Cages and Capsules. *Chem. Soc. Rev.* **2015**, *44*, 586–602.
- (5) Zheng, G.; Price, W. S. Direct Hydrodynamic Radius Measurement on Dissolved Organic Matter in Natural Waters Using Diffusion NMR. *Environ. Sci. Technol.* **2012**, *46*, 1675–1680.
- (6) Wilkins, D. K.; Grimshaw, S. B.; Receveur, V.; Dobson, C. M.; Jones, J. A.; Smith, L. J. Hydrodynamic Radii of Native and Denatured Proteins Measured by Pulse Field Gradient NMR Techniques. *Biochemistry* **1999**, *38*, 16424–16431.

- (7) Bülow, S. v.; Siggel, M.; Linke, M.; Hummer, G. Dynamic Cluster Formation Determines Viscosity and Diffusion in Dense Protein Solutions. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 9843–9852.
- (8) Altieri, A. S.; Hinton, D. P.; Byrd, R. A. Association of Biomolecular Systems Via Pulsed Field Gradient NMR Self-Diffusion Measurements. *J. Am. Chem. Soc.* **1995**, *117*, 7566–7567.
- (9) Weingärtner, H. The Microscopic Basis of Self Diffusion - Mutual Diffusion Relationships in Binary Liquid Mixtures. *Ber. Bunsen.-Ges.* **1990**, *94*, 358–364.
- (10) Muñoz-Muñoz, Y. M.; Guevara-Carrion, G.; Llano-Restrepo, M.; Vrabec, J. Lennard-Jones Force Field Parameters for Cyclic Alkanes from Cyclopropane to Cyclohexane. *Fluid Phase Equilib.* **2015**, *404*, 150–160.
- (11) Bonnaud, P.; Nieto-Draghi, C.; Ungerer, P. Anisotropic United Atom Model Including the Electrostatic Interactions of Benzene. *J. Phys. Chem. B* **2007**, *111*, 3730–3741.
- (12) Padilla, P.; Toxvaerd, S. Self-Diffusion in n-Alkane Fluid Models. *J. Chem. Phys.* **1991**, *94*, 5650–5654.
- (13) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, U.K., 1987.
- (14) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill Professional: United States, 1987.
- (15) Mostinsky, I. L. Diffusion Coefficient. A-to-Z Guide to Thermodynamics, Heat and Mass Transfer, and Fluids Engineering, <http://www.thermopedia.com/de/content/696/>. 2006.
- (16) Wang, J. H. Self-Diffusion and Structure of Liquid Water. II. Measurement of Self-Diffusion of Liquid Water with O18 as Tracer. *J. Am. Chem. Soc.* **1951**, *73*, 4181–4183.

- (17) Copley, J. R. D.; Lovesey, S. W. The Dynamic Properties of Monatomic Liquids. *Rep. Prog. Phys.* **1975**, *38*, 461.
- (18) Weingärtner, H. Chapter 3. NMR Studies of Self-Diffusion in Liquids. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **1994**, *91*, 37–69.
- (19) Mills, R. Search for Isotope Effects in the Self-Diffusion of Benzene and Cyclohexane at 25°. *J. Phys. Chem.* **1975**, *79*, 852–853.
- (20) Freer, R.; Sherwood, J. N. Diffusion in Organic Liquids. Part 2.-Isotope-Mass Effects in Self-Diffusion in Benzene and Cyclohexane. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1030–1037.
- (21) Stejskal, E. O.; Tanner, J. E. Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem. Phys.* **1965**, *42*, 288–292.
- (22) Guevara-Carrion, G.; Janzen, T.; Muñoz-Muñoz, Y. M.; Vrabec, J. Mutual Diffusion of Binary Liquid Mixtures Containing Methanol, Ethanol, Acetone, Benzene, Cyclohexane, Toluene, and Carbon Tetrachloride. *J. Chem. Phys.* **2016**, *144*, 124501.
- (23) Li, J.; Liu, H.; Hu, Y. A Mutual-Diffusion-Coefficient Model Based on Local Composition. *Fluid Phase Equilib.* **2001**, *187-188*, 193–208.
- (24) Liu, X.; Vlugt, T. J.; Bardow, A. Predictive Darken Equation for Maxwell-Stefan Diffusivities in Multicomponent Mixtures. *Ind. Eng. Chem. Res.* **2011**, *50*, 10350–10358.
- (25) Hardt, A. P.; Anderson, D. K.; Rathbun, R.; Mar, B. W.; Babb, A. L., Self-Diffusion in Liquids II: Comparison Between Mutual and Self-Diffusion Coefficients. *J. Phys. Chem.* **1959**, *63*, 2059–2061.
- (26) McCall, D. W.; Douglass, D. C. Diffusion in Binary Solutions. *J. Phys. Chem.* **1967**, *71*, 987–997.

- (27) Iloukhani, H.; Rezaei-Sameti, M.; Zarei, H. Volumetric and Viscometric Studies of Molecular Interaction of the Ternary System Toluene (1)+Cyclohexane (2)+n-Hexane (3) at 298.15 K. *Thermochim. Acta* **2005**, *438*, 9–15.
- (28) Aoyagi, K.; Albright, J. G. Tracer Diffusion and Viscosity Study at 25° in Binary and Ternary Liquid Systems. *J. Phys. Chem.* **1972**, *76*, 2572–2577.
- (29) Hawlicka, E.; Reimschüssel, W. Component Self-Diffusion in Liquid Binary Solutions. *Ber. Bunsen.-Ges.* **1981**, *85*, 210–214.
- (30) Kessler, D.; Witte, H.; Weiss, A. Diffusion of Spherical or Almost Spherical Molecules in the Liquid Phase. II. Liquid Mixtures. *Ber. Bunsen.-Ges.* **1969**, 368–376.
- (31) Mills, R. The Intradiffusion and Derived Frictional Coefficients for Benzene and Cyclohexane in Their Mixtures at 25°. *J. Phys. Chem.* **1965**, *69*, 3116–3119.
- (32) Kamal, I.; McLaughlin, E. Self-Diffusion in Binary Non-Electrolyte Mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1762.
- (33) Merzliak, T.; Bartussek, I.; Stapf, S.; Voda, M. A.; Blümich, B.; Pfennig, A. Description of Intra-Diffusion in Liquid Mixtures. *Fluid Phase Equilib.* **2006**, *245*, 158–167.
- (34) Reimschüssel, W.; Hawlicka, E. Self-Diffusion in Benzene-Toluene and Benzene-Cyclohexane Solutions. *Ber. Bunsen.-Ges.* **1977**, *81*, 1221–1224.
- (35) Ghai, R. K.; Dullien, F. A. L. Diffusivities and Viscosities of Some Binary Liquid Nonelectrolytes at 25°. *J. Phys. Chem.* **1974**, *78*, 2283–2291.
- (36) Pickup, S.; Blum, F. D. Self-Diffusion of Toluene in Polystyrene Solutions. *Macromolecules* **1989**, *22*, 3961–3968.
- (37) Mijaković, M.; Polok, K. D.; Kežić, B.; Sokolić, F.; Perera, A.; Zoranić, L. A Comparison of Force Fields for Ethanol–Water Mixtures. *Mol. Simul.* **2015**, *41*, 699–712.

- (38) Iwahashi, M.; Kasahara, Y. Effects of Molecular Size and Structure on Self-Diffusion Coefficient and Viscosity for Saturated Hydrocarbons Having Six Carbon Atoms. *Journal of Oleo Science* **2007**, *56*, 443–448.
- (39) Guevara-Carrion, G.; Vrabec, J.; Hasse, H. Prediction of Self-Diffusion Coefficient and Shear Viscosity of Water and Its Binary Mixtures with Methanol and Ethanol by Molecular Simulation. *J. Chem. Phys.* **2011**, *134*, 074508.
- (40) Perez, S.; Guevara-Carrion, G.; Hasse, H.; Vrabec, J. Mutual Diffusion in the Ternary Mixture of Water + Methanol + Ethanol and Its Binary Subsystems. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3985–4001.
- (41) Chung, K.-C.; Yu, H.-Y.; Ahn, S.-D. Convection Effects on PGSE-NMR Self-Diffusion Measurements at Low Temperature: Investigation Into Sources of Induced Convective Flows. *Bull. Korean Chem. Soc.* **2011**, *32*, 1970–1974.
- (42) Connell, M. A.; Davis, A. L.; Kenwright, A. M.; Morris, G. A. NMR Measurements of Diffusion in Concentrated Samples: Avoiding Problems with Radiation Damping. *Anal. Bioanal. Chem.* **2004**, *378*, 1568–1573.
- (43) Wu, D. H.; Chen, A.; Johnson, C. S. Flow Imaging by Means of 1D Pulsed-Field-Gradient NMR with Application to Electroosmotic Flow. *J. Magn. Reson., Ser. A* **1995**, *115*, 123–126.
- (44) Hurd, R. E.; Deese, A.; Johnson, M.; Sukumar, S.; van Zijl, P. Impact of Differential Linearity in Gradient-Enhanced NMR. *J. Magn. Reson., Ser. A* **1996**, *119*, 285–288.
- (45) Holz, M.; Heil, S. R.; Sacco, A. Temperature-Dependent Self-Diffusion Coefficients of Water and Six Selected Molecular Liquids for Calibration in Accurate ^1H NMR PFG Measurements. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4740–4742.

- (46) Connell, M. A.; Bowyer, P. J.; Adam Bone, P.; Davis, A. L.; Swanson, A. G.; Nilsson, M.; Morris, G. A. Improving the Accuracy of Pulsed Field Gradient NMR Diffusion Experiments: Correction for Gradient Non-Uniformity. *J. Magn. Reson.* **2009**, *198*, 121–131.
- (47) Sawall, M.; von Harbou, E.; Moog, A.; Behrens, R.; Schröder, H.; Simoneau, J.; Steimers, E.; Neymeyr, K. Multi-Objective Optimization for an Automated and Simultaneous Phase and Baseline Correction of NMR Spectral Data. *J. Magn. Reson.* **2018**, *289*, 132–141.
- (48) Carman, P. C.; Stein, L. H. Self-Diffusion in Mixtures. Part 1. Theory and Its Application to a Nearly Ideal Binary Liquid Mixture. *Trans. Faraday Soc.* **1956**, *52*, 619–627.
- (49) Hirschfelder, J. O.; Curtiss, C. F. The Theory of Flame Propagation. *J. Chem. Phys.* **1949**, *17*, 1076–1081.
- (50) Curtiss, C. F.; Hirschfelder, J. O. Transport Properties of Multicomponent Gas Mixtures. *J. Chem. Phys.* **1949**, *17*, 550–555.
- (51) McCarty, K. P.; Mason, E. A. Kirkendall Effect in Gaseous Diffusion. *Phys. Fluids* **1960**, *3*, 908.
- (52) Miller, L.; Carman, P. C. Self-Diffusion in Mixtures. Part 4.-Comparison of Theory and Experiment for Certain Gas Mixtures. *Trans. Faraday Soc.* **1961**, *57*, 2143–2150.
- (53) Wei, I. C.; Rowley, R. L. Binary Liquid Mixture Viscosities and Densities. *J. Chem. Eng. Data* **1984**, *29*, 332–335.
- (54) Hafez, M.; Hartland, S. Densities and Viscosities of Binary Systems Toluene-Acetone and 4-Methyl-2-pentanone-acetic Acid at 20, 25, 35, and 45 °C. *J. Chem. Eng. Data* **1976**, *21*, 179–182.

- (55) Nikam, P. S.; Jagdale, B. S.; Sawant, A. B.; Hasan, M. Densities and Viscosities of Binary Mixtures of Toluene with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, and 2-Methylpropan-2-ol at (303.15, 308.15, 313.15) K. *J. Chem. Eng. Data* **2000**, *45*, 559–563.
- (56) Windmann, T.; Linnemann, M.; Vrabec, J. Fluid Phase Behavior of Nitrogen + Acetone and Oxygen + Acetone by Molecular Simulation, Experiment and the Peng–Robinson Equation of State. *J. Chem. Eng. Data* **2014**, *59*, 28–38.
- (57) Stephan, S.; Horsch, M. T.; Vrabec, J.; Hasse, H. MolMod – An Open Access Database of Force Fields for Molecular Simulations of Fluids. *Mol. Simul.* **2019**, *45*, 806–814.
- (58) Rutkai, G.; Köster, A.; Guevara-Carrion, G.; Janzen, T.; Schappals, M.; Glass, C. W.; Bernreuther, M.; Wafai, A.; Stephan, S.; Kohns, M.; Reiser, S.; Deublein, S.; Horsch, M.; Hasse, H.; Vrabec, J. ms2: A Molecular Simulation Tool for Thermodynamic Properties, Release 3.0. *Comput. Phys. Commun.* **2017**, *221*, 343–351.
- (59) Green, M. S. Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids. *J. Chem. Phys.* **1954**, *22*, 398–413.
- (60) Kubo, R. Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems. *J. Phys. Soc. Jpn.* **1957**, *12*, 570–586.
- (61) Zwanzig, R. Time-Correlation Functions and Transport Coefficients in Statistical Mechanics. *Annu. Rev. Phys. Chem.* **1965**, *16*, 67–102.
- (62) Janzen, T.; Vrabec, J. Diffusion Coefficients of a Highly Nonideal Ternary Liquid Mixture: Cyclohexane–Toluene–Methanol. *Ind. Eng. Chem. Res.* **2018**, *57*, 16508–16517.

- (63) Lustig, R. Angle-average for the powers of the distance between two separated vectors. *Mol. Phys.* **1988**, *65*, 175–179.
- (64) Flyvbjerg, H.; Petersen, H. G. Error Estimates on Averages of Correlated Data. *J. Chem. Phys.* **1989**, *91*, 461–466.
- (65) Suárez-Iglesias, O.; Medina, I.; de los Ángeles Sanz, M.; Pizarro, C.; Bueno, J. L. Self-Diffusion in Molecular Fluids and Noble Gases: Available Data. *J. Chem. Eng. Data* **2015**, *60*, 2757–2817.
- (66) Zeidler, M. D. Umorientierungszeiten, Sprungzeiten und Quadrupolkopplungskonstanten in Einigen Organischen Flüssigkeiten aus Kernmagnetischen Relaxationszeitmessungen. *Ber. Bunsen.-Ges.* **1965**, *69*, 659–669.
- (67) Goldammer, E. V.; Zeidler, M. D. Molecular Motion in Aqueous Mixtures with Organic Liquids by NMR Relaxation Measurements. *Ber. Bunsen.-Ges.* **1969**, 4–15.
- (68) Krüger, G. J.; Weiss, R. Diffusion Coefficients of Organic Liquids. *Z. Naturforsch., A* **1970**, *25*, 777–780.
- (69) O'Reilly, D. E.; Peterson, E. M. Self-Diffusion Coefficients and Rotational Correlation Times in Polar Liquids. II. *J. Chem. Phys.* **1971**, *55*, 2155–2163.
- (70) Claessens, M.; Fiasse, P.; Fabre, O.; Zimmermann, D.; Reisse, J. Experimental and Theoretical Study of Diffusion in Pure Liquids and Solutions. *Nouv. J. Chim.* **1984**, 357–363.
- (71) Le Bihan, D.; Breton, E. In Vivo Magnetic Resonance Imaging of Diffusion. *C. R. Acad. Sci., Ser. II* **1985**, 1109–1112.
- (72) Le Bihan, D.; Breton, E.; Lallemand, D.; Grenier, P.; Cabanis, E.; Laval-Jeantet, M. MR Imaging of Intravoxel Incoherent Motions: Application to Diffusion and Perfusion in Neurologic Disorders. *Radiology* **1986**, *161*, 401–407.

- (73) Canet, D.; Diter, B.; Belmajdoub, A.; Brondeau, J.; Boubel, J.; Elbayed, K. Self-Diffusion Measurements Using a Radiofrequency Field Gradient. *J. Magn. Reson.* **1989**, *81*, 1–12.
- (74) Holz, M.; Mao, X.; Seiferling, D.; Sacco, A. Experimental Study of Dynamic Isotope Effects in Molecular Liquids: Detection of Translation–Rotation Coupling. *J. Chem. Phys.* **1996**, *104*, 669–679.
- (75) Viel, S.; Ziarelli, F.; Pagès, G.; Carrara, C.; Caldarelli, S. Pulsed Field Gradient Magic Angle Spinning NMR Self-Diffusion Measurements in Liquids. *J. Magn. Reson.* **2008**, *190*, 113–123.
- (76) O'Reilly, D. E.; Peterson, E. M. Self-Diffusion Coefficients and Rotational Correlation Times in Polar Liquids. III. Toluene. *J. Chem. Phys.* **1972**, *56*, 2262–2266.
- (77) Fischer, J.; Weiss, A. Transport Properties of Liquids. V. Self Diffusion, Viscosity, and Mass Density of Ellipsoidal Shaped Molecules in the Pure Liquid Phase. *Ber. Bunsen.-Ges.* **1986**, *90*, 896–905.
- (78) Harris, K. R.; Alexander, J. J.; Goscinska, T.; Malhotra, R.; Woolf, L. A.; Dymond, J. H. Temperature and Density Dependence of the Selfdiffusion Coefficients of Liquid n-Octane and Toluene. *Mol. Phys.* **1993**, *78*, 235–248.
- (79) Mischler, E.; Humbert, F.; Canet, D. A One-shot Diffusion Sequence Using a B1 Gradient. *J. Magn. Reson., Ser. B* **1995**, *109*, 121–125.
- (80) Birkett, J. D.; Lyons, P. A. Diffusion in Deuterio-Normal Hydrocarbon Mixtures. *J. Phys. Chem.* **1965**, *69*, 2782–2783.
- (81) Kulkarni, M. V.; Allen, G. F.; Lyons, P. A. Diffusion in Carbon Tetrachloride-Cyclohexane Solutions. *J. Phys. Chem.* **1965**, *69*, 2491–2493.

- (82) McCool, M. A.; Woolf, L. A. Self-Diffusion Measurements Under Pressure with a Diaphragm Cell: Theory of the Method, and Experimental Results for Cyclohexane. *High Temp.-High Pressures* **1972**, 85–95.
- (83) Freer, R.; Sherwood, J. N. Diffusion in Organic Liquids. Part 1.-Appraisal of a Gel Sectioning Technique and Its Application to Self-Diffusion in Benzene and Cyclohexane. *J. Chem. Soc., Faraday Trans. 1* **1980**, 76, 1021.
- (84) Kato, T. Determination of Velocity Correlation Coefficients in Aqueous Solutions of 2-Butoxyethanol by Quasi-Elastic Light Scattering, Pulsed-Gradient FT-NMR, and Rayleigh-Brillouin Scattering. *J. Phys. Chem.* **1985**, 89, 5750–5755.
- (85) Holz, M.; Weingartner, H. Calibration in Accurate Spin-Echo Self-Diffusion Measurements Using ^1H and Less-Common Nuclei. *J. Magn. Reson.* **1991**, 92, 115–125.
- (86) Piton, M. C.; Gilbert, R. G.; Chapman, B. E.; Kuchel, P. W. Diffusion of Oligomeric Species in Polymer Solutions. *Macromolecules* **1993**, 26, 4472–4477.
- (87) Todica, M.; Guillermo, A.; Pop, A. V.; Damian, G.; Ciurchea, D. Magnetic Field Gradient NMR Measurements of the Self-Diffusion Coefficient of the Small Molecules. *Stud. Univ. Babes-Bolyai, Phys.* **1994**, 3–11.
- (88) Malveau, C.; Diter, B.; Humbert, F.; Canet, D. Self-Diffusion Measurements by Carbon-13 NMR Using Radiofrequency Field Gradients. *J. Magn. Reson.* **1998**, 130, 131–134.
- (89) Tofts, P. S.; Lloyd, D.; Clark, C. A.; Barker, G. J.; Parker, G. J. M.; McConville, P.; Baldock, C.; Pope, J. M. Test Liquids for Quantitative MRI Measurements of Self-Diffusion Coefficient In Vivo. *Magn. Reson. Med.* **2000**, 43, 368–374.
- (90) Kato, H.; Saito, T.; Nabeshima, M.; Shimada, K.; Kinugasa, S. Assessment of Diffusion

- Coefficients of General Solvents by PFG-NMR: Investigation of the Sources Error. *J. Magn. Reson.* **2006**, *180*, 266–273.
- (91) Partington, J. R.; Hudson, R. F.; Bagnall, K. W. Self-Diffusion of Aliphatic Alcohols. *Nature* **1952**, *169*, 583–584.
- (92) Graupner, K.; Winter, E. R. S. 201. Some Measurements of the Self-Diffusion Coefficients of Liquids. *J. Chem. Soc.* **1952**, 1145–1150.
- (93) Johnson, P. A.; Babb, A. L. Liquid Diffusion of Non-Electrolytes. *Chem. Rev.* **1956**, *56*, 387–453.
- (94) Powles, J. G.; Cutler, J. G. Proton Magnetic Resonance Relaxation and Self-Diffusion in the Primary Alcohols at 25°. *Arch. Sci.* **1959**, 135–140.
- (95) Rathbun, R. E.; Babb, A. L. Self-Diffusion in Liquids III: Temperature Dependence in Pure Liquids. *J. Phys. Chem.* **1961**, *65*, 1072–1074.
- (96) Uminski, T.; Dera, J.; Kupryszewski, G. The Measurement of Self-Diffusion Coefficient in Dielectric Liquids Using the Method of Openended Capillaries and Radioisotope Technique. *Acta Phys. Pol.* **1965**, 17–24.
- (97) Rothschild, W. G. Molecular Motion in Liquids: On the Prevalence of Large-Size Rotational and Translational Diffusion Steps. *J. Chem. Phys.* **1970**, *53*, 3265–3271.
- (98) Pratt, K. C.; Wakeham, W. A. Self-Diffusion in Water and Monohydric Alcohols. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 997.
- (99) Hurle, R. L.; Eastal, A. J.; Woolf, L. A. Self-Diffusion in Monohydric Alcohols Under Pressure. Methanol, Methan(2H)ol and Ethanol. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 769.
- (100) Nelson, D. J.; Brammer, C. N. Toward Consistent Terminology for Cyclohexane Conformers in Introductory Organic Chemistry. *J. Chem. Educ.* **2011**, *88*, 292–294.

- (101) Asprion, N.; Hasse, H.; Maurer, G. Thermodynamic and IR Spectroscopic Studies of Solutions with Simultaneous Association and Solvation. *Fluid Phase Equilib.* **2003**, *208*, 23–51.

Figure TOC.1: For Table of Contents use only. Daniel Bellaire, Hendrik Kiepfer, Kerstin Münnemann, Hans Hasse: PFG-NMR and MD simulation study of self-diffusion coefficients of binary and ternary mixtures containing cyclohexane, ethanol, acetone and toluene.