Diffusion Coefficients at Infinite Dilution of Carbon Dioxide and Methane in Water, Ethanol, Cyclohexane, Toluene, Methanol, and Acetone: A PFG-NMR and MD Simulation Study

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Abstract

Diffusion coefficients at infinite dilution are important basic data for all processes involving mass transfer. They can be obtained from studying samples in equilibrium using nuclear magnetic resonance spectroscopy with pulsed field gradients (PFG-NMR), a technique which is widely used in chemistry but is only rarely applied in engineering studies. This advantageous technique was employed here to measure the self-diffusion coefficients of diluted solutions of carbon dioxide and methane in the pure solvents water, ethanol, cyclohexane, toluene, methanol, and acetone at 298.15 K. For the systems (carbon dioxide + water) and (carbon dioxide + ethanol), measurements were also carried out at 308.15 K, 318.15 K and 333.15 K. Except for (methane + water) and (methane + toluene), no literature data for the methane-containing systems were previously available. At the studied solute concentrations, there is practically no difference between the self-diffusion coefficient and the mutual diffusion coefficient. The experimental results are compared to experimental literature data as well as to results from semi-empirical methods for the prediction of diffusion coefficients at infinite dilution. Furthermore, molecular dynamics simulations were carried out for all systems to determine the diffusion coefficient at infinite dilution based on

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Preprint submitted to Journal of Chemical Thermodynamics *October 22, 2021*

force fields that were taken from the literature, and the results are compared to the experimental data and those from the classical prediction methods.

Keywords: Diffusion coefficient, infinite dilution, NMR, molecular simulation

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1. Introduction

Diffusion is an omnipresent phenomenon and is described using diffusion coefficients. There are different types of diffusion coefficients: (i) mutual (or transport) diffusion coefficients and (ii) self-diffusion coefficients. The former are used for describing the mass transport in mixtures, which is important for many processes in nature and technology, the latter describe the Brownian motion of the individual molecules in pure components and mixtures, which is an important basic material property. Two ways of describing mass transfer are well-established: the Fickian approach and that of Maxwell-Stefan, with corresponding diffusion coefficients. At infinite dilution, the differences between the Fickian and the Maxwell-Stefan mutual diffusion coefficients as well as the self-diffusion coefficient of the solute vanish. Therefore, in this study, for the description of mutual and self-diffusion at infinite dilution, the term ‘diffusion coefficient at infinite dilution’ is used without any further specification.

There are many technical processes in which the diffusing component is so dilute that the diffusion coefficient at infinite dilution can be used directly for describing the mass transport. This applies, e.g., to many absorption processes. Furthermore, methods exist that enable the prediction of diffusion coefficients at finite concentrations from those at infinite dilution [1, 2, 3]. All this makes data on diffusion coefficients at infinite dilution particularly valuable.

Compared to their significance, reliable data on diffusion coefficients at infinite dilution are still rare. One major reason for this is that measuring diffusion coefficients in general, and diffusion coefficients at infinite dilution in particular, is tedious: most available methods require carrying out non-equilibrium measurements. In contrast, nuclear magnetic resonance spectroscopy using pulsed field gradients (PFG-NMR) yields information on the self-diffusion coefficient from equilibrium measurements, which greatly facilitates the study. With the PFG-NMR method, diffusion coefficients can be measured with high accuracy [4]. While the method is well established in chemistry and physics, it is still not widely adopted in engineering.

In this work, diffusion coefficients at infinite dilution of the single solutes carbon dioxide (CO_2) and methane (CH_4) in the pure solvents (water, ethanol, cyclohexane, toluene, methanol, and acetone) were determined with PFG-NMR at 298.15 K. Additionally, for the systems (CO_2 + water) and (CO_2 + ethanol), further data at 308.15 K, 318.15 K and 333.15 K were measured. For these systems, a strong enrichment of the solute at the vapor-liquid interface is expected and accurate data on the diffusion coefficient of the solute is needed for evaluating experimental studies on the influence of this enrichment on the mass transfer through the interface [5, 6].

Another goal of this work is to demonstrate the usefulness of PFG-NMR for engineering studies. Consequently, measurements were not only carried out for systems, for which no diffusion coefficients were previously available (all systems with the solute CH_4, except (CH_4 + water)), but also for systems, for which data was available for comparisons. This is in particular the case for the two systems with the solvent water. For (CO_2 + water), abundant data for the diffusion coefficient at infinite dilution are available [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. Fewer data are available for CO_2 in ethanol [35, 10, 11, 36, 37, 29, 38], cyclohexane [39], toluene [10, 40, 41], methanol [35, 10, 11, 19, 31, 42], and acetone [10]. For CH_4, diffusion coefficients have been investigated before in water [8, 43, 9, 44, 45, 46, 47, 48, 34]. For the remaining solvents, only a study on the system (CH_4 + toluene) at 323 K [49] seems to be available.

The methods that were used in the literature for studying the diffusion coefficient can be categorized as follows: diaphragm cells [8], wetted surface absorbers [13, 17], laminar jets [20], capillary cells [29], Taylor dispersion [50, 51], and dynamic light scattering (DLS) [38]. In a diaphragm cell, two solutions of different composition are brought into contact by a diaphragm. The cell usually has to be calibrated with a mixture of known diffusion coefficient. In the wetted surface absorber technique, absorption takes place in a laminar film flowing over a surface of defined geometry, such as a sphere or a wall. The laminar jet method is similar, but the absorption takes place in a free-flowing laminar jet. The two latter methods require knowledge of the fluid dynamics for the analysis. Capillary cells make use of the capillary effect in order to restrict convection. One component is placed in the capillary and then brought into contact with the second component. For studying the diffusion coefficient of a gas in a solvent by the Taylor dispersion technique, a sample of a solution containing the gas and the solvent is injected into a stream of the pure solvent and the dispersion of the gas upon the laminar flow through a capillary is monitored. Dynamic light scattering is able to obtain mutual diffusion coefficients from equilibrated samples. This is accomplished by observing coherent (laser) light being scattered by the sample which is influenced by local concentration fluctuations (i.e. diffusion).

PFG-NMR makes use of magnetic gradient fields which imprint phase shifts on the nuclear spins of the diffusing species resulting in decreasing NMR signals with increasing gradient strength and increasing Brownian motion of the molecules. This way, the molecular motion can be quantified and the self-diffusion coefficient can be extracted [52]. In contrast to the aforementioned methods, the PFG-NMR method does not require any calibration or additional information on the investigated systems.

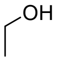
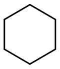
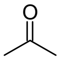
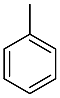
The PFG-NMR data in this work are complemented by molecular simulation studies of the diffusion coefficients in all considered systems as well as by comparisons with results from two semi-empirical methods for the prediction of diffusion coefficients at infinite dilution, namely those of Wilke and Chang [53] and Evans et al. [54].

This paper is organized as follows: First, the PFG-NMR measurements are described, then the semi-empirical methods and the molecular simulations for the prediction of the diffusion coefficient at infinite dilution. In the results section, the experimental data are presented and compared to experimental literature data and the results from the predictions with semi-empirical methods and molecular simulations.

2. Experiments

Table 1 lists the chemicals that were used in this work, their suppliers, and their purities.

Table 1: Overview of chemicals that were used with the respective suppliers and purities. The chemicals were used as provided by the suppliers without further purification.

	Structure	Molar mass	Supplier	Purity
		g·mol^{-1}		mol·mol^{-1}
^{13}C-Carbon dioxide	$O{=}^{13}C{=}O$	45.01	Sigma-Aldrich	0.99
Methane	CH_4	16.04	Air Liquide S.A.	0.99
Water	H_2O	18.01	This work[†]	
Ethanol		46.07	Merck KGaA	0.999
Cyclohexane		84.16	Merck KGaA	0.999
Methanol		32.04	Merck KGaA	0.999
Acetone		58.08	Merck KGaA	0.999
Toluene		92.14	AppliChem GmbH	0.999

[†] Elix Essential 5 Purification System (Merck KGaA), TOC < 30 ppb, resistivity > 5 MΩ·cm.

^{1}H and ^{13}C PFG-NMR spectra were recorded with a Bruker Biospin NMR spectrometer with a magnetic field strength of 9.4 T, corresponding to a proton Larmor frequency of 400.40 MHz, which was equipped with a probe with cryogenically cooled electronics (magnet: Ascend 400; console: Avance III HD 400; probe: CryoProbe Prodigy). The spectrometer's temperature control unit was calibrated with a platinum resistance thermometer (Pt-100) that was, in turn, calibrated using a standard, certified by PTB, Braunschweig. The standard uncertainty of the temperature measurement is estimated to be $u(T) = 0.1$ K. All samples were measured in pressure-tight NMR tubes with valves (5 mm Extreme Series Level 3, Norell). For the measurements involving CO_2, isotope-enriched $^{13}CO_2$ was used, which facilitated the measurement significantly. Due to its slightly higher mass, $^{13}CO_2$ diffuses slower and the experimental self-diffusion coefficients were corrected by Eq. (1) in order to apply the data to $^{12}CO_2$ [55].

$$D_{^{12}\mathrm{CO}_2} = D_{^{13}\mathrm{CO}_2} \sqrt{\frac{M_{^{13}\mathrm{CO}_2}}{M_{^{12}\mathrm{CO}_2}}} \tag{1}$$

All reported CO_2 diffusion coefficients were corrected by Eq. (1) and refer to $^{12}CO_2$. In the rest of the paper, the superscript 12 is omitted, as it is customary. The solvents were filled into the pressure tubes in which they were degassed by applying vacuum. $^{13}CO_2$ or CH_4 was then added and the tube was thermostatted at the target temperature. The amount of the gas was adjusted so that the desired total pressure in the thermostatted sample was reached. These conditions were maintained until the dissolution process was finished, which was checked by NMR measurements.

The NMR measurements were carried out using a stimulated spin-echo pulse sequence with bipolar pulsed gradients as implemented in the spectrometer's software (pulse sequence: `stebpgp1s`) [56]. The experimental data was evaluated using the Stejskal-Tanner equation [52]. This equation was modified to compensate for gradient non-linearity as well as the application of bipolar gradient pulses, resulting in Eq. (2); details are reported elsewhere [4].

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

I is the signal intensity, I_0 is the signal intensity without gradient, γ is the gyromagnetic ratio of the measured nucleus, δ is the duration of the gradient pulse, Δ is the diffusion time, τ is a correction constant that is applied when bipolar gradient pulses are used, and g is the gradient strength. c_n (in this case c_1 and c_2) are probe-specific fit coefficients correcting for gradient non-linearity which have been determined through calibration measurements on samples with well-known self-diffusion coefficients. The number for the diffusion coefficient D_i is determined from a fit of Eq. (2) to experimental data for I and I_0.

The experimental parameters were chosen as follows: $\Delta = 50$ ms, $\tau = 0.2$ ms. The gradient strength g was incremented from 2.5 to 48.5 G$\cdot$cm^{-1} in 8 steps with 32 scans for ^{1}H and 16 scans for ^{13}C measurements, respectively. The pre-scan delay and gradient pulse duration δ were adjusted to the respective sample in order to facilitate sufficient sample relaxation and diffusion encoding, respectively. With the described parameters, the measurement time per sample ranged between one and four hours, which depended on the respective sample's relaxation time. Lower experimental time spans are possible with a slight decrease in accuracy. It should be noted that the described experiments were carried out on equilibrated samples.

This study aims at determining the diffusion coefficient at infinite dilution. Therefore, measurements were carried out at low solute concentrations. The mole fraction of dissolved gas in the solvent was determined by direct integration of the respective peaks in the recorded 1D NMR spectra. Phase and baseline correction were applied using the processing tool developed by Sawall et al. [57]. Three measurements at different low solute mole fractions were carried out for each mixture in order to be able to detect any concentration-dependence of the self-diffusion coefficient. The mixtures were produced by applying 0.1, 0.2 and 0.4 MPa of solute gas pressure to the solvent. The pressure was maintained throughout the equilibration and measurement process. The mole fractions of the diffusing component were below 0.01 mol$\cdot$mol^{-1} for CH_4 and 0.04 mol$\cdot$mol^{-1} for CO_2, except for (CO_2 + acetone), where the highest CO_2 mole fraction was 0.07 mol/mol. As an example, the self-diffusion coefficients of CO_2 and CH_4 in toluene at 298.15 K are shown in Fig. 1. Within the limits given by the experimental uncertainty of the diffusion coefficients, no concentration dependence of the measured self-diffusion coefficients can be discerned. The experimental uncertainty is dominated by the uncertainty of the fit by Eq. 2. Similar results were obtained for all other mixtures except (CO_2 + acetone) where a slight concentration dependence was observed. Therefore, the data for (CO_2 + acetone) were extrapolated linearly towards infinite dilution and the resulting intercept is reported as the diffusion coefficient at infinite dilution $D_i^{\infty,\mathrm{exp}}$ with i indicating the solute. For all other mixtures investigated in this work, the arithmetic mean of the three measurements at low solute mole fractions is reported. For the system (CO_2 + water), where the solute and the solvent only exhibit either proton or carbon atoms (oxygen was not measured), no direct determination of the solute mole fraction from the NMR spectrum is possible. Therefore, the solute pressure was used instead of the mole fraction to check the concentration-dependence as well as to determine the diffusion coefficient at infinite dilution. The expanded, relative uncertainty is estimated as $U_\mathrm{r}(D_i^{\infty,\mathrm{exp}}) = 0.05$ ($k = 2$) with k being a coverage factor. For the system (CO_2 + water), the expanded, relative uncertainty is estimated as $U_\mathrm{r}(D_i^{\infty,\mathrm{exp}}) = 0.1$ ($k = 2$) based on a literature comparison.

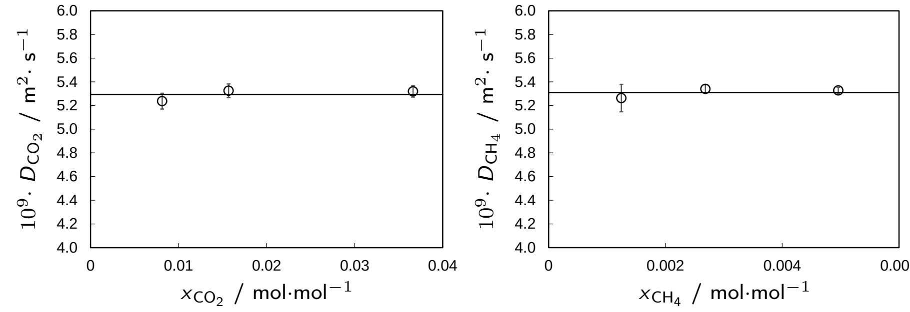


Figure 1: Self-diffusion coefficients D_i of CO_2 (left) and CH_4 (right) in toluene at 298.15 K at three different mole fractions, respectively. The line indicates the arithmetic average number.

3. Semi-empirical methods for predicting the diffusion coefficient at infinite dilution

Several methods for the prediction of diffusion coefficients at infinite dilution have been reported in the literature, many of which are based on the Stokes-Einstein equation [58, 59, 60, 61]. One of the most frequently used methods is that of Wilke and Chang (WC) [53], which is given by Eq. (3).

$$(D_i^{\infty,\mathrm{WC}}/\mathrm{m}^2\cdot\mathrm{s}^{-1}) = \frac{7.4\cdot 10^{-12}\sqrt{\phi_\mathrm{solvent}(M_\mathrm{solvent}/\mathrm{g}\cdot\mathrm{mol}^{-1})}\,(T/\mathrm{K})}{(\eta_\mathrm{solvent}/\mathrm{cP})(v_i/\mathrm{cm}^3\cdot\mathrm{mol}^{-1})^{0.6}} \tag{3}$$

Here, $D_i^{\infty,\mathrm{WC}}$ is the predicted diffusion coefficient at infinite dilution, M_solvent is the molar mass of the solvent, T is the temperature, η_solvent is the dynamic viscosity, v_i is the liquid molar volume of solute i at its normal boiling point and ϕ_solvent is the so-called association factor of the solvent.

More recently, Evans et al. have proposed a method that is given by Eq. (4) [54]. It is abbreviated as SEGWE (Stokes-Einstein-Gierer-Wirtz Estimation) by the authors which hints at the two equations from which it was derived, namely the Stokes-Einstein equation and an equation by Gierer and Wirtz [62].

$$\begin{gathered}(D_i^{\infty,\mathrm{SEGWE}}/\mathrm{m}^2\cdot\mathrm{s}^{-1}) = \frac{(k_B/\mathrm{J}\cdot\mathrm{K}^{-1})(T/\mathrm{K})\left[\frac{3\alpha}{2}+\frac{1}{1+\alpha}\right]}{6\pi(\eta_\mathrm{solvent}/\mathrm{Pa}\cdot\mathrm{s})\sqrt[3]{\frac{3(M_i/\mathrm{g{\cdot}mol}^{-1})}{4\pi(\rho_\mathrm{eff}/\mathrm{g{\cdot}m}^{-3})(N_\mathrm{A}/\mathrm{mol}^{-1})}}}\\ \alpha = \sqrt[3]{\frac{(M_\mathrm{solvent}/\mathrm{g}\cdot\mathrm{mol}^{-1})}{(M_i/\mathrm{g}\cdot\mathrm{mol}^{-1})}}\end{gathered} \tag{4}$$

M_i is the molar mass of solute i, k_B is Boltzmann's constant and N_A is Avogadro's constant. $\rho_\mathrm{eff} = 619$ kg·m^{-3} is an effective density whose value was fitted to literature data by the method's authors. Data for the dynamic viscosity η_solvent were taken from DIPPR [63]. From the same database, data for the liquid molar volume of the solutes v_i at their normal boiling point were obtained, which are needed in the Wilke-Chang method. Furthermore, Wilke-Chang requires data for the association factor of the solvent ϕ_solvent. In this work, this parameter was obtained from a fit to all available data on diffusion coefficients at infinite dilution in the Dortmund Data Bank [64]. CO_2 has no normal boiling point, due to its high triple point pressure. Therefore, the liquid molar volume of CO_2 at the triple point was used instead. The numerical values for v_i and ϕ_{solvent} used in this work are summarized in Table A.1 in the appendix.

4. Molecular Simulation

Molecular dynamics (MD) simulations were performed using molecular models of the studied components that were taken from the literature. All models belong to the class of rigid multi-center Lennard-Jones (LJ) models with superimposed electrostatic interaction sites: CH_4 [65], CO_2 [66], water [67], ethanol [68], cyclohexane [69], toluene [70], methanol [71] and acetone [72]. Most of these models stem from previous works of our group. The water model is known as TIP4P-water and one of the most widely used water models. There are many more molecular models for the substances that were considered here, but as our main focus was on the PFG-NMR experiments, it was out of the scope of the present work to make a more comprehensive study of these molecular models. The unlike interaction parameters were calculated using the Lorentz-Berthelot combining rules, given in Eqs. (5) and (6) [73]:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{5}$$

$$\epsilon_{ij} = \xi\sqrt{\epsilon_i \epsilon_j} \tag{6}$$

where σ_{ij} and ϵ_{ij} are the length and energy parameters describing the interactions between unlike LJ sites i and j and σ_i, σ_j, ϵ_i and ϵ_j are the corresponding parameters of the interactions between sites of the same type. The parameter ξ can be adjusted to binary data but was set to $\xi = 1$ throughout the present work, except for the system (CO_2 + ethanol), as explained in more detail in the results section. All simulations were carried out using the simulation package *ms*2 (version 3.0.0) [74]. The pure component input files were taken from the MolMod model data base [75].

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 x 10^5

equilibration steps and 5 x 10^5 production steps. The obtained density was then used in a canonical ensemble (NVT) simulation at the same temperature and composition. Here, 3 x 10^5 equilibration steps and 10^6 production steps were utilized in order to sample the velocity autocorrelation function. The self-diffusion coefficients of all components in the mixture were calculated with the Green-Kubo formalism [76, 77, 78, 79, 80]:

$$D_i = \frac{1}{3N_i} \int_0^\infty \left\langle \sum_{k=1}^{N_i} \mathbf{v}_{i,k}(0) \cdot \mathbf{v}_{i,k}(t) \right\rangle dt \tag{7}$$

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 2.92 fs and the sampling length of the autocorrelation functions, which are used to calculate the self-diffusion coefficient, was 58.5 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 Lustig [81] 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 [82].

In order to obtain a reliable value for the diffusion coefficient at infinite dilution, the solute mole fraction was set to $x_\mathrm{i} = 0.001$ mol·mol^{-1}. It is known from previous studies that this is sufficient to determine numbers for the diffusion coefficient at infinite dilution without the need for an extrapolation.

5. Results and Discussion

Fig. 2 gives an overview of the results for the diffusion coefficients at infinite dilution of CO_2 and CH_4 dissolved in water, ethanol, cyclohexane, toluene, methanol, and acetone at 298.15 K that were obtained in the present work by experiments and molecular simulations. The results are compared to results from the two semi-empirical methods for the prediction of diffusion coefficients at infinite dilution described above, which are labeled here simply as Wilke-Chang (Eq. (3)) and SEGWE (Eq. (4)). The corresponding numerical results are presented in Table 2.

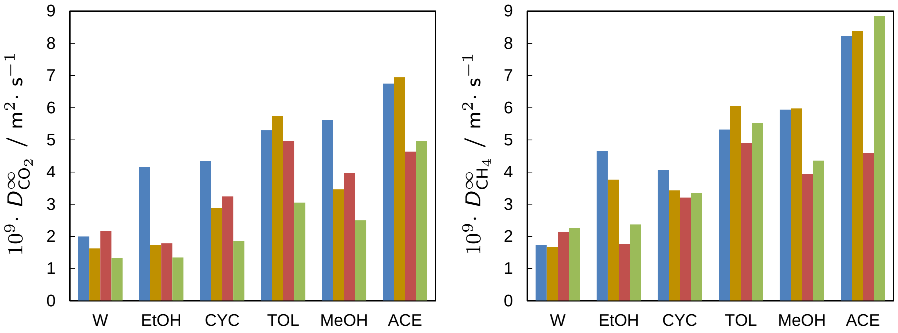


Figure 2: Comparison of diffusion coefficients at infinite dilution D_i^{∞} of CO_2 (left) and CH_4 (right) dissolved in water (W), ethanol (EtOH), cyclohexane (CYC), toluene (TOL), methanol (MeOH) and acetone (ACE) at 298.15 K. Data from the present work from experiments (blue) and molecular simulations (yellow) are compared to predictions from semi-empirical methods: Wilke-Chang (red) and SEGWE (green).

The diffusion coefficients of CO_2 at infinite dilution in the different studied solvents increase in the order: water, ethanol, cyclohexane, toluene, methanol, acetone. That order is basically the same for the solute CH_4, except for the fact that ethanol and cyclohexane are interchanged. Moreover, the diffusion coefficients at infinite dilution of the two solutes in the same solvent do not differ much. This illustrates the predominant role of the solvent for the diffusion of light-boiling solutes. The similarities are quite astonishing considering the fact that the solutes differ considerably in size, mass, and electrostatic properties (CH_4 is non-polar while CO_2 has a strong quadrupole moment). The low values of the diffusion coefficient at infinite dilution that are found for water are a consequence of the strong hydrogen-bonding network of water. When comparing the diffusion coefficients in methanol and ethanol, two opposing effects on the

Table 2: Diffusion coefficients at infinite dilution (no distinction between mutual and self-diffusion, cf. text) for CO_2 and CH_4 dissolved in water, ethanol, cyclohexane, toluene, methanol and acetone from experiments ($D_i^{\infty,\mathrm{exp}}$, exp. rel. uncertainty $U_r(D_i^{\infty,\mathrm{exp}}) = 0.05$ ($k = 2$), for (CO_2 + water): $U_r(D_i^{\infty,\mathrm{exp}}) = 0.1$ ($k = 2$)), molecular simulation ($D_i^{\infty,\mathrm{sim}}$, last digit uncertainty in parentheses), as well as from two semi-empircial methods: Wilke-Chang, cf. Eq. (3) ($D_i^{\infty,\mathrm{WC}}$) and SEGWE, cf. Eq (4) ($D_i^{\infty,\mathrm{SEGWE}}$). Temperature standard uncertainty: $u(T) = 0.1$ K.

	T	$D_i^{\infty,\mathrm{exp}}$	$D_i^{\infty,\mathrm{sim}}$	$D_i^{\infty,\mathrm{WC}}$	$D_i^{\infty,\mathrm{SEGWE}}$
Solvent	K	10^{-9} $\mathrm{m^2{\cdot}s^{-1}}$			
			CO_2		
Water	298.15	2.00	1.6(2)	2.17	1.33
	308.15	2.70	1.2(2)	2.77	1.69
	318.15	3.49	2.3(2)	3.46	2.11
	333.15	4.02	2.8(3)	4.67	2.85
Ethanol	298.15	4.16	1.7(4)	1.78	1.34
	308.15	5.23	1.2(5)	2.22	1.67
	318.15	5.88	3.5(6)	2.74	2.06
	333.15	7.24	2.9(5)	3.68	2.77
Cyclohexane	298.15	4.35	2.9(6)	3.24	1.85
Toluene	298.15	5.30	5.7(7)	4.96	3.05
Methanol	298.15	5.62	3.5(4)	3.98	2.50
Acetone	298.15	6.75	6.9(9)	4.64	4.97
			CH_4		
Water	298.15	1.73	1.7(3)	2.15	2.26
Ethanol	298.15	4.65	3.8(9)	1.76	2.37
Cyclohexane	298.15	4.07	3.4(12)	3.21	3.34
Toluene	298.15	5.32	6.1(13)	4.91	5.52
Methanol	298.15	5.94	6.0(6)	3.93	4.35
Acetone	298.15	8.23	8.4(14)	4.58	8.84

solute mobility must be considered: the hydrogen-bonding strength on the one side and the size and mass of the solvent on the other, where the latter prevails. Comparing the results for the solvents cyclohexane and toluene, which have a similar size and mass, one finds higher diffusion coefficients in toluene, probably due to the fact that the voids created by the rigidity of toluene facilitate the diffusion of the small solutes. The highest diffusion coefficients are found in the solvent acetone, which is comparatively small, not self-associating, and has only a moderately strong dipole.

Figs. 3 and 4 give an overview of the available literature data for the studied systems. For the systems with CH_4, a comparison with literature data is only possible for (CH_4 + water) and for (CH_4 + toluene) (cf. Supplementary Material), for all other systems, no data on the diffusion coefficient at infinite dilution could be found in the literature.

Abundant literature data are available for the systems (CO_2 + water) and (CH_4 + water). Also, for the systems (CO_2 + methanol), (CO_2 + ethanol) and (CO_2 + toluene) literature data from several sources are available. The literature data often scatter considerably. The width of the band in which data for a given system and temperature are found is typically of the order of 10^{-9} m^2 · s^{-1}, which is far above the uncertainty that is reported for the individual data sets. The range of the reported uncertainties varies considerably for some of the methods. The uncertainties are on average about $u_r = 0.03$ which is comparable to the uncertainty of the PFG-NMR measurements in this work. Average uncertainties of $u_r = 0.03$ are reported for studies employing wetted surface absorbers (range over all references: $0.02 - 0.05$) and capillary cells. Higher uncertainties are typically reported for studies using diaphragm cells (average $u_r = 0.06$, range: $0.035 - 0.1$) and lower uncertainties are reported for laminar jet (average $u_r = 0.01$, range: $0.003 - 0.02$) and Taylor dispersion measurements ($u_r = 0.02$).

Excellent agreement between the results from the present work and literature data (Fig. 3) is found for the systems (CO_2 + cyclohexane), for which only one data set is available in the literature; (CO_2 + toluene), for which the present

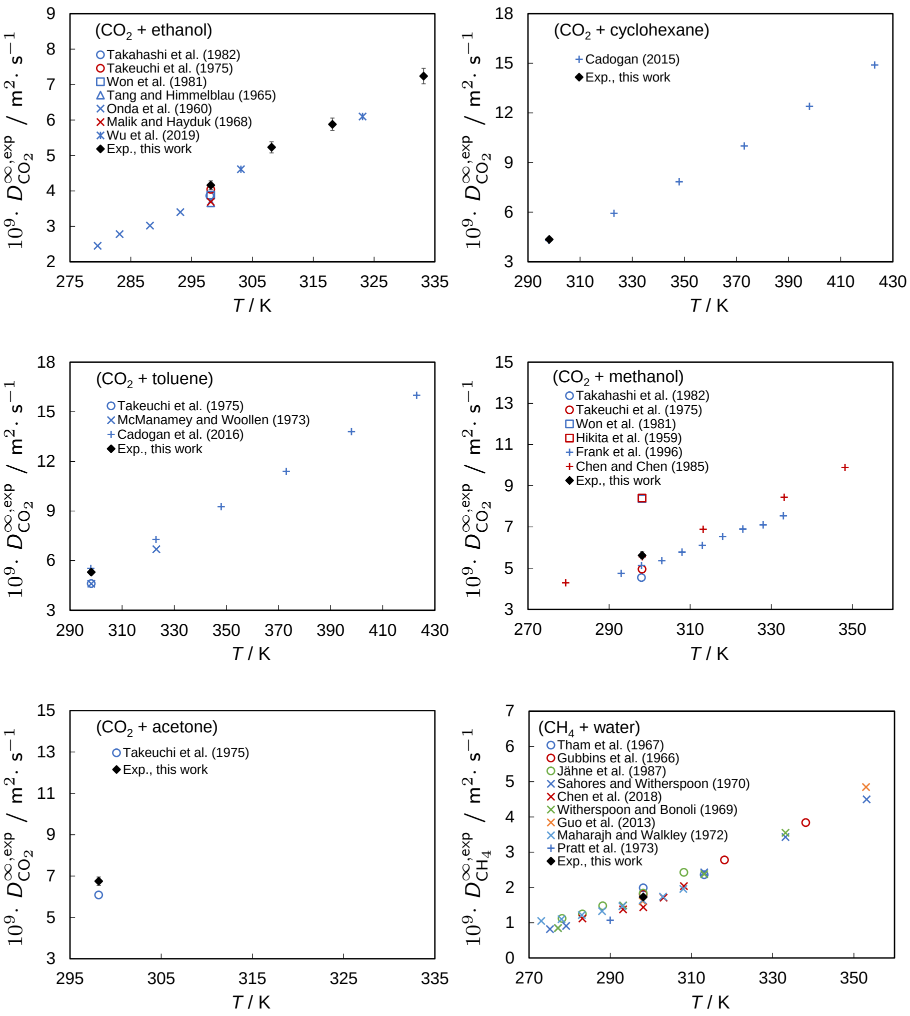


Figure 3: Comparison of experimental data from the present work for diffusion coefficients at infinite dilution $D_i^{\infty,\mathrm{exp}}$ of CO_2 and CH_4 in different solvents with literature data [35, 10, 11, 36, 37, 29, 39, 10, 40, 41, 35, 10, 11, 19, 31, 42, 10, 8, 43, 9, 44, 45, 46, 47, 48, 38, 34], grouped by the used experimental method. Circles: Diaphragm cell, squares: Wetted surface absorber, triangle: Laminar jet, crosses: Capillary cell, pluses: Taylor dispersion, stars: Dynamic light scattering. Error bars are only given for the experiments from the present work for clarity. If they are not indicated, they are within the symbol size.

data basically confirm the recent data of Cadogan et al. [41]; and (CH_4 +

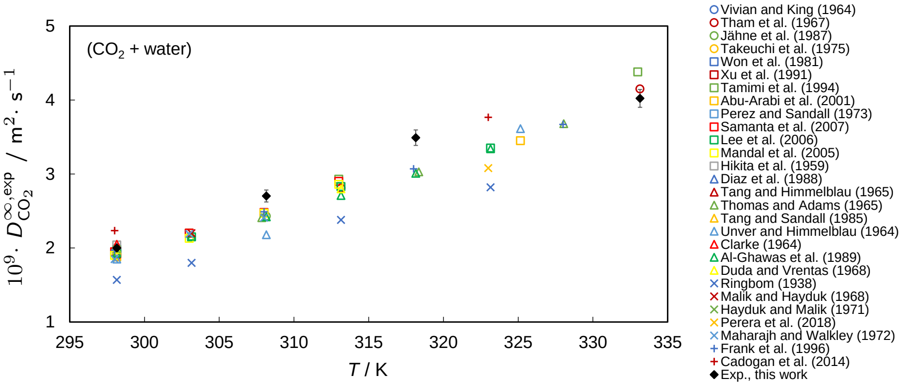


Figure 4: Comparison of experimental data from the present work for diffusion coefficients at infinite dilution $D_i^{\infty,\mathrm{exp}}$ of CO_2 in water with literature data [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34], grouped by the used experimental method. Circles: Diaphragm cell, squares: Wetted surface absorber, triangle: Laminar jet, crosses: Capillary cell, pluses: Taylor dispersion. Error bars are only given for the experiments from the present work for clarity. If they are not indicated, they are within the symbol size.

water), for which the present data lie in the middle of the scattering set of literature data. For (CO_2 + acetone) only a single data point is available for comparison, which is lower than the present result by about 10 %. For (CO_2 + methanol) the data of the present work seem to confirm those of Chen and Chen [42]. For (CO_2 + ethanol) the data from the present work lie at the upper end of the band of the literature data but the agreement is still well within the combined uncertainties of the data. The results for the system (CO_2 + water), cf. Fig. 4, are difficult to interpret. At 298.15 K the present results are well within the band of the literature data, for 308.15 K and 318.15 K they lie above that band, while for 333.15 K they lie slightly below that band.

In a gross picture, when comparing the results from the PFG-NMR to those from other methods, the former tend to lie rather on the upper end of the band of results than at the lower. All in all, the comparison with the literature data shows that the PFG-NMR method is an attractive option for measuring diffusion coefficients at infinite dilution due to its ease of application and good accuracy.

In the following, the experimental results from the present work are compared to the results from the different prediction methods, cf. Fig. 2 and Table 2. For characterizing the deviations, we use the norm of the relative deviation δ, cf. Eq. (8).

$$\delta = \frac{|D_i^{\infty,\mathrm{exp}} - D_i^{\infty,m}|}{D_i^{\infty,\mathrm{exp}}} \tag{8}$$

where m denotes the prediction method. The three studied methods for predicting the diffusion coefficients yield non-uniform results. For the system (CH_4 + toluene), all three methods yield good results (δ below 15 %). Fair results are also obtained for the systems (CH_4 + cyclohexane) as well as for both systems in which the solvent is water (δ mostly below 25 %). Comparing the predictions of the two semi-empirical methods, it is found that Wilke-Chang does a significantly better job for the systems containing CO_2, while the performance of both methods is generally similar for the systems containing CH_4, with the exception of the system (CH_4 + acetone) for which the prediction of Wilke-Chang is poor.

It is interesting to see that the predictions from the molecular simulations are on average better than those from the semi-empirical methods. The molecular simulation results were obtained without using information on the mixtures, based only on the pure component models, except for the system (CO_2 + ethanol), for which a ξ-value was used that was fitted to VLE data in a previous work [5]. This led to an improvement of the prediction of the diffusion coefficient of about 21 % compared to the case with $\xi = 1$. It is remarkable that the molecular simulation results for all systems with CH_4 are good (average δ of 9 %). For the systems with CO_2, good predictions are achieved for water, toluene, and acetone, but not for the two alcohols methanol and ethanol, or for cyclohexane. Poor predictions of diffusion coefficients in systems with alcohols in molecular simulations with the models that were used here (as well as with similar models) have been observed before [4, 83, 84, 70].

For the systems (CO_2 + water) and (CO_2 + ethanol), further measurements were carried out at 308.15 K, 318.15 K and 333.15 K. The results for these two systems are shown in Fig. 5, which contains also corresponding results from the molecular simulations and the two semi-empirical methods. It is evident that all predictions underestimate the experimental diffusion coefficient, with only a single exception: the prediction of Wilke-Chang for (CO_2 + water). The temperature-dependence of the experimental data is predicted fairly well by the semi-empirical methods as well as by the molecular simulations, but all in all, except for Wilke-Chang for (CO_2 + water), none of the considered methods yields good results. This is particularly true of the system (CO_2 + ethanol), for which the predicted values are often less than half of the experimental values. The data from the molecular simulations at different temperatures do not lie on a straight line. We have reproduced the individual simulations and were unable to reveal the reason for this unexpected scattering.

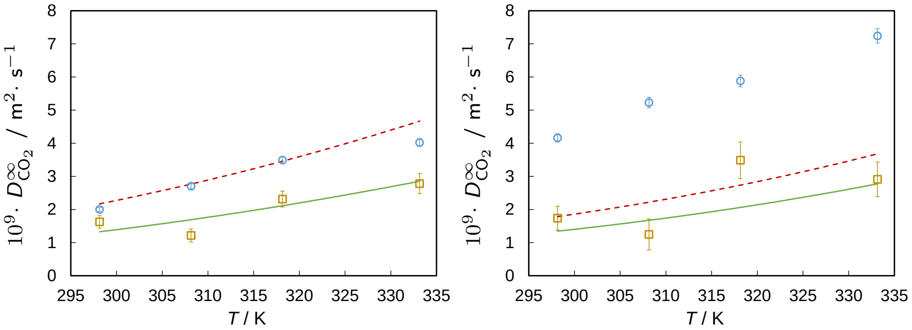


Figure 5: Diffusion coefficients at infinite dilution of CO_2 ($D^\infty_{CO_2}$) dissolved in water (left) and in ethanol (right) as a function of temperature from experiments (blue circles), molecular simulation (yellow squares), as well as from two semi-empircial methods: Wilke-Chang, cf. Eq. (3) (red broken line) and SEGWE, cf. Eq (4) (green line).

6. Conclusions

The diffusion coefficients at infinite dilution of CO_2 and CH_4 dissolved in water, ethanol, cyclohexane, toluene, methanol, and acetone were determined by

PFG-NMR at 298.15 K. For the systems (CO_2 + water) and (CO_2 + ethanol), also measurements at (308.15 K, 318.15 K, 333.15 K) were carried out. A comparison with literature data, where available, confirmed the reliability of the experimental results. Furthermore, the experimental data were compared to MD simulation data as well as semi-empirical methods for the prediction of diffusion coefficients at infinite dilution [53, 54]. The diffusion coefficients of CH_4 in all solvents were predicted well by the molecular simulations using molecular models from the literature. The same holds for the diffusion coefficient of CO_2 in water, toluene and acetone. However, the predictions of the diffusion coefficient of CO_2 in the alcohols by the molecular simulations was found to be poor. The studied semi-empirical methods for the prediction of diffusion coefficients at infinite dilution generally gave poorer predictions than the molecular simulations, especially for the CH_4 containing systems. The temperature dependence of the diffusion coefficients of CO_2 in water and ethanol is predicted fairly well by all methods while, however, underestimating the experimental data. Remarkably, for (CO_2 + water), the method of Wilke and Chang [53] yields an excellent prediction over almost the whole temperature range.

Concluding, this study provides accurate experimental data for diffusion coefficients at infinite dilution for CO_2 and CH_4 dissolved in widely-used solvents. The results demonstrate that PFG-NMR, while in principle only applicable for measuring self-diffusion coefficients, is also an attractive technique for measuring mutual diffusion coefficients of diluted components. The measurements can be performed in equilibrium and yield results that are at least as accurate as those obtained with classical non-equilibrium measurements. Furthermore, it demonstrates that molecular models are attractive for predicting diffusion coefficients even if the models were not trained to such data.

7. Acknowledgments

The authors gratefully acknowledge funding of the present work by the ERC Advanced Grant ENRICO (grant agreement No. 694807). The simulations were

carried out on the ELWE supercomputer at Regional University Computing Center Kaiserslautern (RHRK) under the Grant TUK-MTD.

8. Appendix

Table A.1 lists the numerical values of the parameters v_i and ϕ_{solvent} which are used in the Wilke-Chang method for the prediction of diffusion coefficients at infinite dilution in this work. v_i was obtained from DIPPR [63]. For CO_2, the value at the triple point is used (also from DIPPR [63]). ϕ_{solvent} was obtained through a fit of the Wilke-Chang method to all available data of diffusion coefficients at infinite dilution in the Dortmund Data Bank [64].

Table A.1: Numerical values of the liquid molar volume v_i and the solvent association factor ϕ_{solvent} which are used in the Wilke-Chang method in this work.

	v_i	ϕ_{solvent}
	$\text{cm}^3{\cdot}\text{mol}^{-1}$	-
Water		3.44
Ethanol		1.27
Cyclohexane		1.57
Toluene		1.30
Methanol		2.25
Acetone		0.55
CO_2	37.27	
CH_4	37.97	

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