Diffusion Coefficients in Mixtures of Poly(oxymethylene) Dimethyl Ethers (OME) with Alkanes

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Abstract

Poly(oxymethylene) dimethyl ethers (OME, $CH_3O(CH_2O)_nCH_3$) are new synthetic fuels that can be produced from renewable resources. An interesting application of OME fuels is using them in mixtures with hydrogenated vegetable oils (HVO), which mainly consist of alkanes. Data on diffusion coefficients of OME containing mixtures are lacking in the literature, but are needed for modelling OME production processes and OME combustion. Therefore, in the present work self-diffusion coefficients of binary mixtures of OME and alkanes were measured by pulsed field gradient nuclear magnetic resonance (PFG-NMR). OME with chain lengths $n = 1...4$ were studied; the alkanes were *n*-dodecane (C12) and *n*-hexadecane (C16). The measurements in the binary mixtures were carried out at high dilution of the diffusing components and extrapolated to obtain the self-diffusion coefficients at infinite dilution that are identical with the mutual diffusion coefficient. For completeness, also the self-diffusion coefficients of the pure components were measured. The experiments were carried out at temperatures between 298.15 and 353.15 K at ambient pressure. The experimental data for the diffusion coefficients at infinite dilution were compared to results from established prediction methods (SEGWE, Wilke and Chang), revealing considerable discrepancies. Furthermore, entropy scaling (ES) was applied here for the first time for modeling diffusion coefficients at infinite dilution. By coupling the results from entropy scaling with the Vignes equation, mutual diffusion coefficients in mixtures of OME and alkanes can be predicted now as a function of the temperature, pressure and composition for a wide range of conditions.

Introduction

Blends of poly(oxymethylene) dimethyl ethers (OME) and hydrogenated vegetable oils (HVO) are interesting new synthetic fuels that can be produced from renewable resources.[1–4] OME are oligomers with the chemical structure $CH_3O(CH_2O)_nCH_3$ with $n \geq 2$. For synthetic fuels OME with chain lengths $n = 3 - 5$ are often used.[5] These oligomers have suitable physical properties to replace fossil diesel, but produce much less soot upon combustion because they contain oxygen in their backbone.[6–8] HVO consist predominantly of *n*-alkanes, with C-numbers between 15 and 20.[8] For the modelling of production processes and combustion applications, information and models for the transport properties of OME and HVO and their mixtures are required. They are needed, e.g., for calculating the Lewis number *Le*, which is the ratio of the heat conductivity and the diffusion coefficient, which must be known to decide whether explosions of droplets in fuel sprays may occur.[9,10]

There are several types of diffusion coefficients. The self-diffusion coefficient characterizes the mobility of individual molecules, whereas the mutual diffusion coefficient describes the mobility of the collectives of molecules. Mutual diffusion coefficients are needed for the description of mass transport on a macroscopic scale. Mutual diffusion is commonly described either by the Maxwell-Stefan or the Fickian framework. The corresponding diffusion coefficients are related by the thermodynamic factor.[11] At infinite dilution of the diffusing component in a binary mixture, the self-diffusion coefficient, the Maxwell-Stefan diffusion coefficient and the Fickian diffusion coefficient are identical. Interpolation schemes exist that enable the prediction of diffusion coefficients at finite concentrations form those at infinite dilution, the most widely used of which is that of Vignes et al.[12]

Pulsed field gradient nuclear magnetic resonance (PFG-NMR) is an excellent method for measuring self-diffusion coefficients and, by extrapolation, also information on the diffusion coefficients at infinite dilution can be obtained. While PFG-NMR measurements of diffusion coefficients are common in the natural sciences, they have been applied only occasionally in engineering studies.[13–15] Compared to other physico-chemical properties, experimental data on diffusion coefficients is relatively scarce in the literature.[16] Therefore, many empirical methods have been developed for their prediction. They generally refer to the state of infinite dilution. For an overview, see e.g. Poling et al.[17] In the present study, we use the fairly recent model of Evans et al.[18] (SEGWE) as well as the well-established method of Wilke and Chang (WC)[19] for comparisons with the new data presented here.

Transport properties can also be modeled based on entropy scaling (ES). The basic idea behind this approach is that the considered transport property can be transformed in a way so that it becomes a univariate function of the configurational entropy.[20,21] The entropy can be calculated as a function of state variables such as temperature and pressure, e.g. from equations of state (EOS).[22,23] Entropy scaling has been applied multiple times in the literature for modeling the thermal conductivity, the shear viscosity as well as self-diffusion coefficients in pure components.[24–27] Entropy scaling has also been applied for modeling the viscosity and thermal conductivity of mixtures. Furthermore, diffusion coefficients at infinite dilution have been predicted indirectly based on the Stokes-Einstein theory that was corrected using results from entropy scaling.[28] Yet, to the best of our knowledge, entropy scaling has not yet been applied directly to describe diffusion coefficients in mixtures, i.e. for scaling mixture diffusion coefficients.

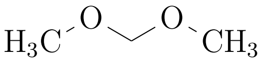
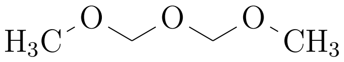
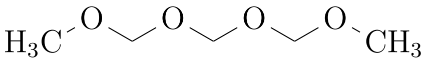
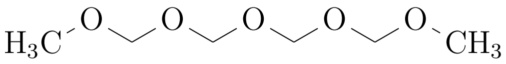
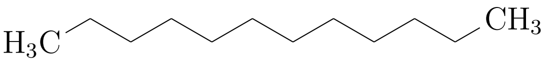
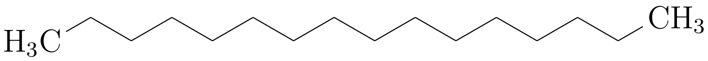
In this work, diffusion coefficients at infinite dilution in binary mixtures of OME_n and alkanes were determined from data obtained by PFG-NMR spectroscopy at temperatures between 298.15 K and 353.15 K at ambient pressure. The results were compared to those from the models of Evans et al.[18] (SEGWE) and Wilke and Chang[19] (WC). An entropy scaling method for predicting diffusion coefficients at infinite dilution was developed and applied to the new data, enabling extrapolations over a wide range of conditions.

Experimental Section

Chemicals and Sample Preparation. Table 1 gives an overview of the chemicals that were used in the present work, their structural formula and their purity. Alkanes and OME_1 were purchased from Sigma Aldrich, $\text{OME}_{2\text{-}4}$ were supplied by BASF SE. The alkanes were used as received, the OME_n were dried with molecular sieve (3Å) before use. The samples were prepared gravimetrically using a laboratory balance (Mettler-Toledo XSR225DU) with an uncertainty of 10^{-5} g. A PTFE syringe filter from Captiva (pore size 0.45 µm) was used to weigh in OME_n in order to trap any debris of the molecular sieve. The total mass of each sample was approximately 5 g, from which the amount needed to fill the NMR tube (about 0.1 g) was taken. The uncertainty of the mole fraction is estimated to be 0.0001 mol mol^{-1} for all components. The concentrations of the diluted component x_i in the studied binary mixtures were approximately $0.005, 0.010, 0.025\,\text{mol mol}^{-1}$.

Measurement of self-diffusion coefficients. The measurements were carried out as in our previous works.[14,15] ^{1}H PFG-NMR measurements were carried out with a NMR spectrometer with a magnetic field strength of 9.4 T corresponding to a proton Larmor frequency of 400.25 MHz that was equipped with a double resonance broad band probe (magnet Ascend 400, console Avance III HD 400, probe BBFO, Bruker Biospin). 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 uncertainty of the

Table 1: Overview of chemicals that were used and their purities.

	Structure	Molar mass / g mol^{-1}	Purity / g g^{-1}
OME$_1$		76.09	0.985
OME$_2$		106.12	0.985
OME$_3$		136.15	0.985
OME$_4$		166.17	0.985
n-dodecane		170.33	0.990
n-hexadecane		226.41	0.990

temperature measurement is 0.1 K. Special sample tubes with an outer diameter of 2.5 mm (Deutero) were used in order to minimize sample convection.[29] The pulse sequence contained bipolar pulsed gradients and was applied as implemented in the NMR spectrometer's software (pulse sequence: stebpgp1s). The self-diffusion coefficient D_i of species i was obtained from a fit of the natural logarithm of the relative NMR signal integral as a function of the squared gradient strength using the Stejskal-Tanner[30] equation:

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

where I is the signal integral, I_0 is the signal integral without gradient, γ is the gyromagnetic ratio, δ is the duration of the gradient pulse, g is the gradient strength, $\mathit{\Delta}$ is the diffusion time, and τ is the correction constant due to the usage of bipolar gradients. Each diffusion experiment consisted of 16 gradient steps with 16 scans each for the pure solvents and 32 scans each for the binary mixtures, respectively, with a prescan delay that was chosen long enough to ensure complete relaxation, resulting in numbers between 10 and 45 s. The gradient pulse duration δ was adjusted to the respective sample between 0.5 and 1.9 ms. The gradient strength g was incremented following a square root relationship from 2.3 to 43.1 G cm^{-1} and the diffusion time $\mathit{\Delta}$ was chosen as 50 ms for all measurements. The time constant τ was chosen as 0.2 ms, corresponding to the time delay between the bipolar gradient lobes. Baseline and phase correction of the spectra were performed manually. All peaks were integrated manually.

Mutual diffusion coefficients at infinite dilution D_{ij}^{∞} were obtained by linear extrapolation of self-diffusion coefficients to infinite dilution of the diffusing component i. In most cases, the results from the three diluted samples agreed within the experimental uncertainty, so that taking the average value would have been sufficient. The relative standard uncertainty for the determination of D_i from the fit to the experimental NMR data using the Stejskal Tanner Eq. (1) was $0.01 \cdot 10^{-9}$ m^{2}s^{-1}. The statistical relative standard uncertainty estimated from the results of three repeated measurements also was $0.01 \cdot 10^{-9}$ m^{2}s^{-1}. We therefore estimate the uncertainty of the diffusion coefficient data measured in the present work to be $0.02 \cdot 10^{-9}$ m^{2}s^{-1}.

Models

Established methods for predicting diffusion coefficients. The SEGWE model of Evans et al.[18] for predicting the diffusion coefficient of solute "1" at infinite dilution in a solvent "2" D_{12}^{∞} is given by

$$D_{12}^{\infty,\,\mathrm{SEGWE}}/\mathrm{m}^2\ \mathrm{s}^{-1} = \frac{\left(k_\mathrm{B}/\mathrm{J\ K}^{-1}\right)\left(T/\ \mathrm{K}\right)\left[\frac{3\alpha}{2} + \frac{1}{1+\alpha}\right]}{6\pi\left(\eta_2/\mathrm{Pa}\cdot\mathrm{s}\right)\sqrt[3]{\frac{3\left(M_1/\mathrm{g\ mol}^{-1}\right)}{4\pi\left(\rho_\mathrm{eff}/\mathrm{g\ m}^{-3}\right)\left(N_\mathrm{A}/\mathrm{mol}^{-1}\right)}}} \tag{2}$$

$$\alpha = \sqrt[3]{\frac{\left(M_2/\mathrm{g\ mol}^{-1}\right)}{\left(M_1/\mathrm{g\ mol}^{-1}\right)}}$$

where k_B is Boltzmann's constant, T is the temperature, η_2 is the dynamic viscosity of the solvent "2", M_1 is the molar mass of the solute "1", M_2 is the molar mass of the solvent "2", $\rho_\mathrm{eff} = 619$ kg m^{-3} is an "effective density", the number of which was fitted to literature data by the authors[18] and N_A is Avogadro's constant.

The model of Wilke and Chang (WC)[19] is given by

$$D_{12}^{\infty,\,\mathrm{WC}}/\mathrm{m}^2\ \mathrm{s}^{-1} = 7.4 \cdot 10^{-12} \frac{\sqrt{\Phi_2 \left(M_2/\mathrm{g\ mol}^{-1}\right)}\,(T/\ \mathrm{K})}{(\eta_2/\mathrm{cP})\left(v_1/\mathrm{cm}^3\ \mathrm{mol}^{-1}\right)^{0.6}} \tag{3}$$

where Φ_2 is the association factor of the solvent "2" which was set to 1 here in all cases, and v_1 is the liquid molar volume of the pure solute "1" at their normal boiling point.[19]

Data for the dynamic viscosity η_2 of alkanes[31,32] and of OME[33,34] were taken from the literature. Data for the liquid molar volume of the solutes at their normal boiling point v_1 were computed from correlations from DIPPR[35] and Burger et al.[1] and are listed in Table S.5 in the Supporting Information.

Entropy Scaling. In this work, entropy scaling was used to model the self-diffusion coefficients of the pure components as well as diffusion coefficients at infinite dilution in binary systems. The latter has, to the best of our knowledge, not been done before. The approach we use here is based on the entropy scaling framework from Schmitt et al.[36] and was used in combination with the PC-SAFT[37] equation of state (EOS). The EOS parameters to model all pure components were taken from the literature, for the alkanes from Gross and Sadowski[37] and for the OME$_n$ from Schappals et al.[38] The self-diffusion coefficients of the pure components were scaled according to Schmitt et al.[36] For applying this framework to the diffusion coefficients at infinite dilution, some modifications were necessary, which are introduced in the following. The Rosenfeld-scaled diffusion coefficient of solute "1" at infinite dilution in solvent "2" $D_{12}^{\infty,+}$ is

$$D_{12}^{\infty,+} = D_{12}^{\infty} \frac{\rho_\mathrm{N}^{1/3}}{\sqrt{RT/M_2}} \left(\frac{-s_\mathrm{conf}}{R}\right)^{2/3} \tag{4}$$

where R is the universal gas constant, M_2 is the molar mass of the solvent "2", ρ_N the number density of the solvent at the given state point, and s_conf the molar configurational entropy of the solvent at the given state point and describes the part of the entropy originating from the interactions of the molecules.

For the zero-density limit, the Chapman-Enskog theory is used, which yields the term given in Eq. (5) for the binary diffusion coefficient[17] in the gas phase and is thus independent of the mole fraction.

$$D^{\infty}_{\mathrm{CE},12} = \frac{3}{8}\sqrt{\frac{RT}{\pi M_{12}}}\frac{1}{\rho_{\mathrm{N}}\sigma_{12}^{2}\Omega_{D}} \tag{5}$$

Herein, M_{12} is a reduced molar mass calculated as $M_{12} = 2/(1/M_1 + 1/M_2)$ from the molar masses of both components M_1 and M_2, σ_{12} is the mean particle size calculated as $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ with σ_1 and σ_2 being parameters describing the particle size of both components "1" and "2", Ω_D is the reduced collision integral for diffusion. The collision integral is a function of the reduced temperature $T\,/\,\varepsilon_{12}k_{\mathrm{B}}^{-1}$, i.e. $\Omega_D = \Omega_D(T\,/\,\varepsilon_{12}k_{\mathrm{B}}^{-1})$. The parameter ε_{12} is an energy parameter of the mixture which is calculated from the pure-component energy parameters ε_1 and ε_2 as $\varepsilon_{12} = \sqrt{\varepsilon_1\varepsilon_2}$. The calculation of the pure component parameters σ_1, σ_2, ε_1 and ε_2 as well as the collision integral Ω_D is based on the Lennard-Jones model[39,40] and is described in Schmitt et al.[36]

The final 'CE-scaled' value of the diffusion coefficient at infinite dilution $\widehat{D}^{+}_{12}$ is given as

$$\widehat{D}^{+}_{12} = \frac{D^{+}_{12}}{D^{+}_{\mathrm{CE},12}}W + \frac{D^{+}_{12}}{\min(D^{+}_{\mathrm{CE},12})}(W-1) \tag{6}$$

where W is a function that realizes the transition from the low-density scaling $D^{+}_{12}/D^{+}_{\mathrm{CE},12}$ to the high-density scaling $D^{+}_{12}/\min(D^{+}_{\mathrm{CE},12})$ (see Schmitt et al.[36] for details).

These scaled diffusion coefficients are expressed as function of the dimensionless configurational entropy $\tilde{s} = -s_{\mathrm{conf}}/(R\,m)$ where m is the chain length parameter of the PC-SAFT equation of state. The function $\widehat{D}^{+}(\tilde{s})$ is given by

$$\ln\left(\widehat{D}^{+}_{12}(\tilde{s})\right) = \frac{\alpha^{(D)}_{2,12}\tilde{s}^{2} + \alpha^{(D)}_{3,12}\tilde{s}^{3}}{1 + g^{(D)}_{1}\ln(\tilde{s}+1) + g^{(D)}_{2}\tilde{s}} \tag{7}$$

where $\alpha^{(D)}_{2,12}$ and $\alpha^{(D)}_{3,12}$ are component-specific parameters fitted to experimental data and $g^{(D)}_{1}$ and $g^{(D)}_{2}$ are global parameters that were fitted to Lennard-Jones simulation data.[36]

The global and component-specific parameters are given in the Supporting Information.

Vignes equation. The Vignes equation[12] for predicting mutual diffusion coefficients in a binary mixture 1 + 2 from the diffusion coefficients at infinite dilution D_{12}^{∞} and D_{21}^{∞} (where the first index indicates the diluted component) is:

$$D_{12} = \left(D_{12}^{\infty}\right)^{x_2} \left(D_{21}^{\infty}\right)^{x_1} \tag{8}$$

Results and discussion

In the following, first the experimental results for the self-diffusion coefficients of the pure components are presented and compared to literature data, wherever this is possible. Then, the results from the entropy scaling model of the self-diffusion coefficients of the pure components are discussed. After this, the experimental results of the self-diffusion coefficients for the binary mixtures are presented, together with their extrapolation to infinite dilution. The results for the diffusion coefficients at infinite dilution are then compared to the SEGWE and the WC model and the application of entropy scaling to the data is discussed.

Pure components. The experimental data of the self-diffusion coefficients of pure alkanes measured in this work are compared to literature data[41–43] in Figure 1 (left). Good agreement is observed. The experimental data for the studied pure OME$_n$ are shown in Figure 1 (right). Due to the low boiling temperature of OME$_1$ ($T^s_{\mathrm{OME}_1} = 315.15\,\mathrm{K}$),[7] the self-diffusion coefficient was measured only at 298.15 K. No literature data of pure OME$_n$ are available for comparison. The data presented in Figure 1 show the expected trends regarding the influence of temperature and molar mass of the components. The numerical experimental data for the pure components measured in this work are given in Table 2.

Figure 1 also shows the results form the modeling of the experimental data by entropy scaling. Good agreement is observed. This is not astonishing as two parameters were fitted to the data for each studied component and the data were measured only in a quite narrow temperature range at ambient pressure. Furthermore, as only the temperature was varied, the entropy scaling brings no immediate advantages for correlating the data set. The advantage of entropy scaling is that based on the limited amount of data that is provided here, self-diffusion coefficients can be predicted for a much wider range of conditions (temperatures, pressures) for all studied components. That such extrapolation yield good results has been demonstrated in extensive studies with model fluids.[26]

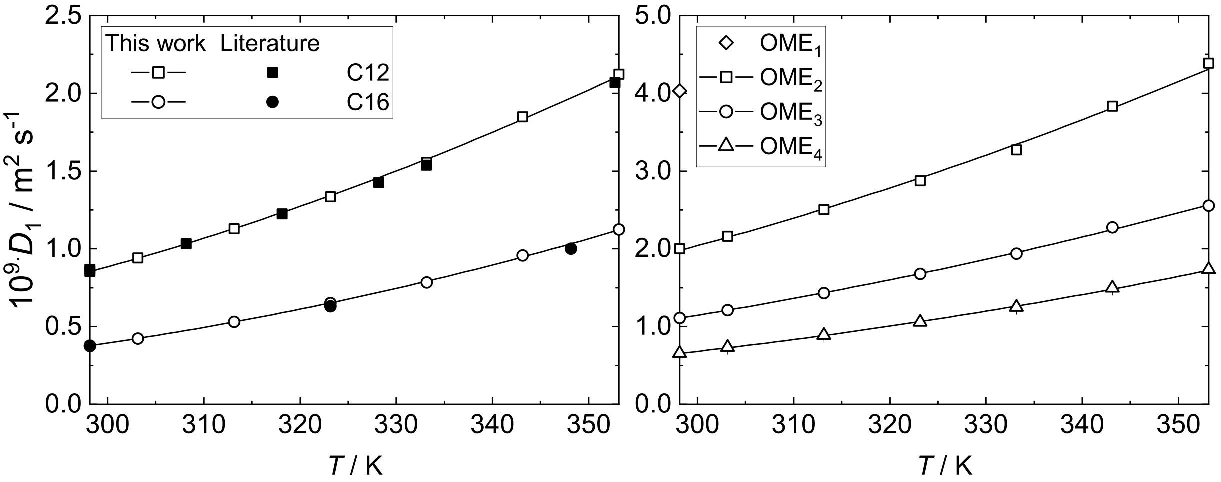


Figure 1: Self-diffusion coefficients of *n*-dodecane (C12) and *n*-hexadecane (C16) (left) and OME$_n$ (right) as a function of temperature. Symbols: experimental results from this work obtained with PFG-NMR spectroscopy (open) and literature data[41–43] (filled). Solid lines: results from entropy scaling. Error bars are within symbol size.

Table 2: Experimental data from PFG-NMR spectroscopy for the self-diffusion coefficients of *n*-dodecane (C12), *n*-hexadecane (C16), and OME$_n$ at ambient pressure. Relative uncertainty of self-diffusion coefficient: $\Delta D_1 = 0.02 \cdot 10^{-9}\,\mathrm{m^2 s^{-1}}$. Uncertainty of temperature: $\Delta T = 0.1\,\mathrm{K}$.

	C12	C16	OME$_1$	OME$_2$	OME$_3$	OME$_4$
T / K			$10^9 \cdot D_1$ / m^{2}s^{-1}			
298.15	0.856	0.376	4.031	2.002	1.113	0.656
303.15	0.942	0.424		2.162	1.212	0.729
313.15	1.128	0.531		2.504	1.431	0.886
323.15	1.334	0.651		2.873	1.678	1.058
333.15	1.557	0.784		3.272	1.937	1.246
343.15	1.848	0.957		3.836	2.278	1.494
353.15	2.122	1.125		4.389	2.553	1.733

Binary mixtures. As an example, Figure 2 shows the experimental data obtained in the present work for the self-diffusion coefficient of OME_1 in binary mixtures with either n-dodecane (C12) or n-hexadecane (C16) at 298.15 K. The results at high concentrations of OME_1 were obtained in measurements to determine the diffusion coefficient of the alkanes in OME_1 and are only shown for completeness. As expected, the self diffusion coefficient of OME_1 is close to that in pure OME_1 in that region.

The addition of the alkane lowers the self-diffusion coefficient of OME_1 and the effect is more important for n-hexadecane than for n-dodecane. In the region of very low OME_1 concentrations that was studied here, the dependency of the OME_1 diffusion coefficient on the OME_1 concentration is almost linear, so that the extrapolation to infinite dilution poses no problem.

The numerical experimental data for the self-diffusion coefficients in binary mixtures measured in this work are given in the Supporting Information. The numerical data for the extrapolated diffusion coefficients at infinite dilution are given in Tables 3 and 4.

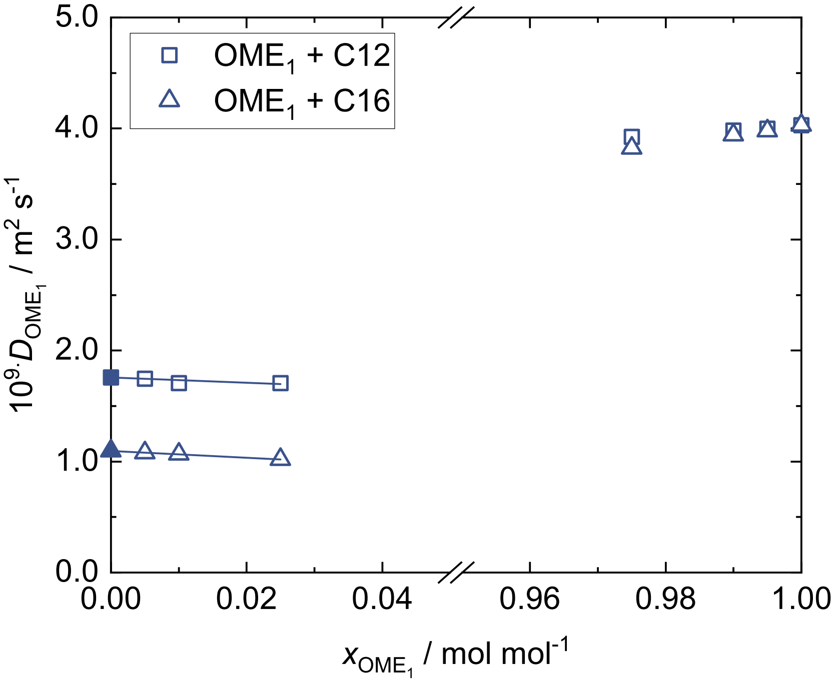


Figure 2: Self-diffusion coefficients of OME_1 as a function of composition in n-dodecane (C12) and n-hexadecane (C16) at 298.15 K. Open symbols: experimental results. Filled symbols: extrapolated results. Solid lines: extrapolation. Error bars are within symbol size.

Figure 3 shows the results for the diffusion coefficients at infinite dilution in binary mixtures of OME_n + n-dodecane (C12) and Figure 4 of OME_n + n-hexadecane (C16) at different temperatures. As expected, the diffusion coefficients of OME_n in n-dodecane are higher than in n-hexadecane and the diffusion coefficients of n-dodecane in a given OME_n are higher than those of n-hexadecane in the same OME_n and the diffusion coefficients increase with increasing temperature.

The correlation of the data for the diffusion coefficients at infinite dilution with entropy scaling was successful for all studied systems. For each pair solute + solvent, two parameters were fitted to the data, so that the success of the correlation is not astonishing, but it should be kept in mind that the method enables extrapolations beyond the range that was studied here.

The predictions with the SEGWE and the WC model yield only poor results. No clear ranking of the models is possible; sometimes SEGWE is better, sometimes WC.

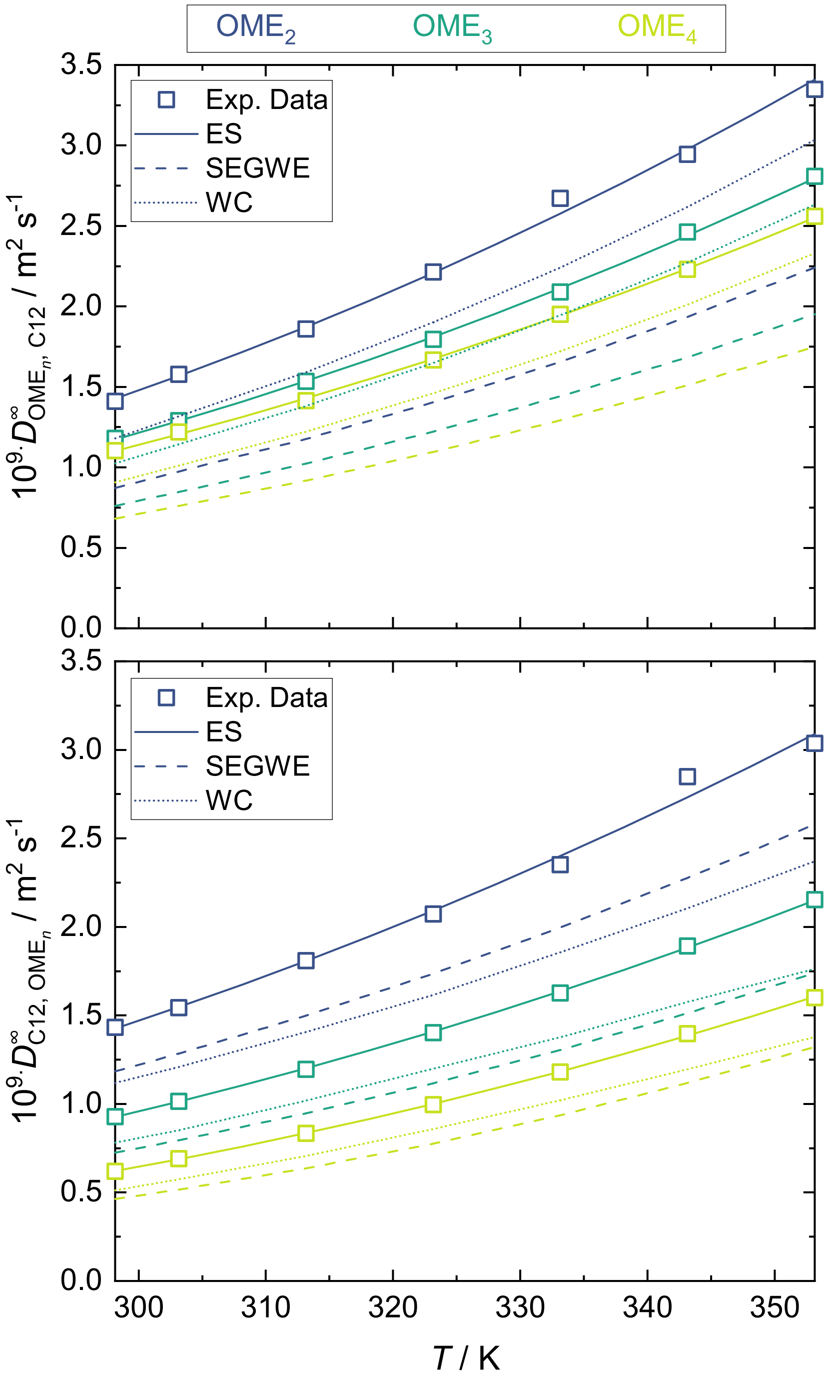


Figure 3: Diffusion coefficients at infinite dilution in binary mixtures of OME$_n$ + n-dodecane (C12) as a function of temperature. Symbols: experimental results from PFG-NMR spectroscopy. Lines: entropy scaling model (solid) and predictions with SEGWE (dashed) and WC (dotted).

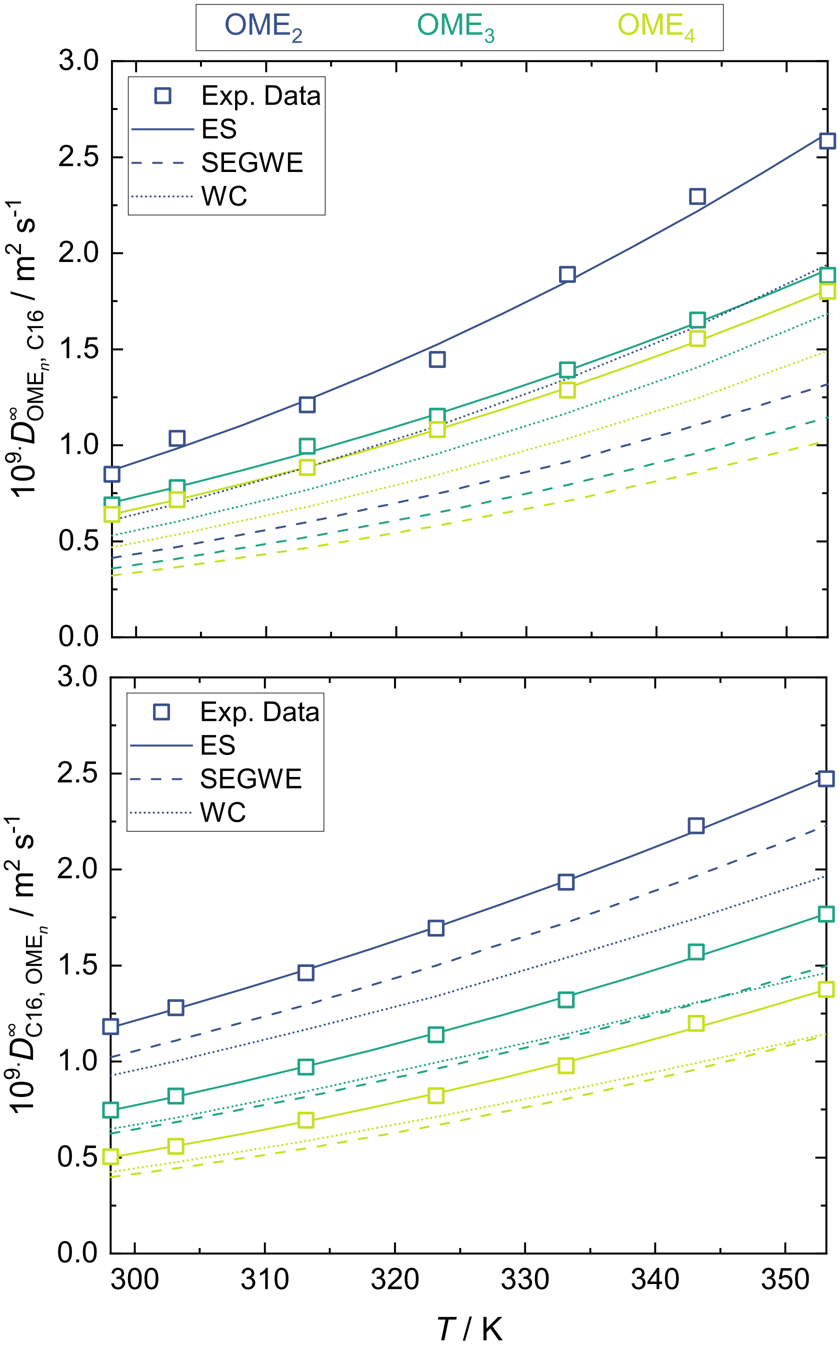


Figure 4: Diffusion coefficients at infinite dilution in binary mixtures of OME_n + n-hexadecane (C16) as a function of temperature. Symbols: experimental results from PFG-NMR spectroscopy. Lines: entropy scaling model (solid) and predictions with SEGWE (dashed) and WC (dotted).

Table 3: Diffusion coefficients of OME_n at infinite dilution in binary mixtures with n-dodecane (C12) and n-hexadecane (C16) at ambient pressure. Relative uncertainty of diffusion coefficient: $\Delta D_1 = 0.02 \cdot 10^{-9}\,\mathrm{m^2s^{-1}}$. Uncertainty of temperature $\Delta T = 0.1\,\mathrm{K}$.

Solute	OME_1	OME_2	OME_3	OME_4	OME_1	OME_2	OME_3	OME_4
Solvent	n-dodecane (C12)				n-hexadecane (C16)			
T / K	$10^9 \cdot D^{\infty}_{\mathrm{OME}n,\mathrm{C12}}$ / $\mathrm{m^2s^{-1}}$				$10^9 \cdot D^{\infty}_{\mathrm{OME}n,\mathrm{C16}}$ / $\mathrm{m^2s^{-1}}$			
298.15	1.759	1.410	1.180	1.104	1.094	0.849	0.690	0.640
303.15		1.579	1.289	1.220		1.036	0.780	0.717
313.15		1.860	1.534	1.415		1.211	0.995	0.885
323.15		2.214	1.796	1.666		1.446	1.151	1.081
333.15		2.673	2.090	1.952		1.890	1.393	1.287
343.15		2.945	2.463	2.230		2.296	1.652	1.555
353.15		3.348	2.807	2.560		2.585	1.885	1.802

Table 4: Diffusion coefficients of n-dodecane (C12) and n-hexadecane (C16) at infinite dilution in binary mixtures with OME_n at ambient pressure. Relative uncertainty of diffusion coefficient: $\Delta D_1 = 0.02 \cdot 10^{-9}\,\mathrm{m^2s^{-1}}$. Uncertainty of temperature: $\Delta T = 0.1\,\mathrm{K}$.

Solute	n-dodecane (C12)				n-hexadecane (C16)			
Solvent	OME_1	OME_2	OME_3	OME_4	OME_1	OME_2	OME_3	OME_4
T / K	$10^9 \cdot D^{\infty}_{\mathrm{C12},\mathrm{OME}n}$ / $\mathrm{m^2s^{-1}}$				$10^9 \cdot D^{\infty}_{\mathrm{C16},\mathrm{OME}n}$ / $\mathrm{m^2s^{-1}}$			
298.15	2.482	1.433	0.929	0.620	2.051	1.181	0.747	0.503
303.15		1.544	1.015	0.691		1.279	0.821	0.559
313.15		1.810	1.196	0.834		1.461	0.971	0.694
323.15		2.207	1.402	0.996		1.694	1.140	0.822
333.15		2.352	1.626	1.180		1.935	1.321	0.979
343.15		2.849	1.893	1.397		2.228	1.571	1.199
353.15		3.037	2.155	1.600		2.472	1.767	1.376

An example for the application of the entropy scaling model based on the new data on diffusion coefficients at infinite dilution from the present work is presented in Figure 5, where the mutual diffusion coefficients in the system OME_2 + n-dodecane (C12) are shown for a wide range of temperatures using the Vignes equation. Therein, the numbers of the diffusion coefficients at infinite dilution outside the temperature range that was studied by experiments here, were obtained from the entropy scaling model. The interpolation by the Vignes equation is almost linear in all cases. The results should be interpreted as predictions of the binary Maxwell-Stefan diffusion coefficient. For calculating Fickian diffusion coefficients, the thermodynamic factor should be considered, which can be calculated for the systems studied here either based on the PC-SAFT equation of state or based on the model of the Gibbs excess energy described in Breitkreuz et al.[8]

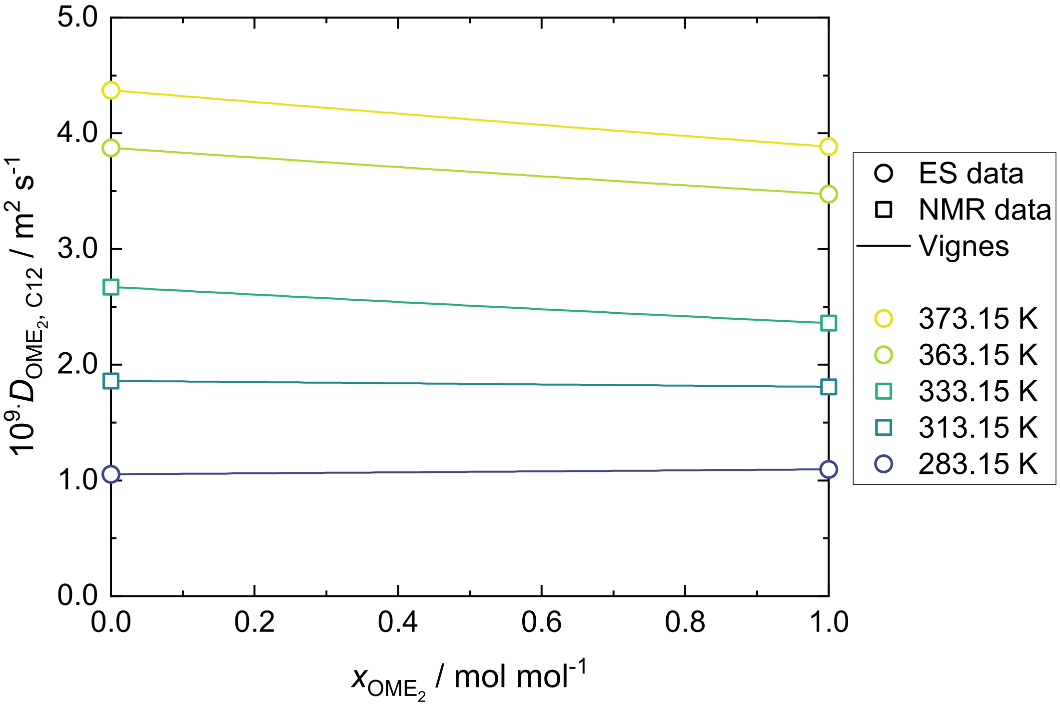


Figure 5: Diffusion coefficients of OME_2 + n-dodecane (C12) as a function of composition and temperature from NMR data, entropy scaling and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Solid lines: Vignes correlation.

Conclusions

The self-diffusion coefficients of the pure components n-dodecane, n-hexadecane and OME_n ($n = 1 \ldots 4$) as well as self-diffusion coefficients in binary mixtures of an OME_n with (n-dodecane or n-hexadecane) were measured at temperatures between 298.15 and 353.15 K with PFG-NMR. From the binary data, the diffusion coefficients at infinite dilution in the studied systems were determined. The comparison with literature data for the pure alkanes confirmed the reliability of the experimental method. It was found that two well established methods for predicting diffusion coefficients from the literature (SEGWE, Wilke and Chang) yield only poor predictions for the studied systems. The new data were used to train models based on entropy scaling in connection with the PC-SAFT equation of state. This method was applied here for the first time to diffusion coefficients at infinite dilution. The entropy scaling models describe the experimental data very well and are expected to yield reliable predictions also far outside the range in which they were fitted. The information on the diffusion coefficients at infinite dilution can be combined with the Vignes model for predicting mutual diffusion coefficients in binary mixtures as a function of the temperature, pressure and composition. Also methods for extending this approach to multicomponent mixtures exist.[44] The new results enable modeling of phenomena such as droplet explosions[9] during the combustion of mixtures of OME and HVO, which are interesting renewable synthetic fuels.

Supporting Information Available

The Supporting Information is available free of charge at *Link*. Numerical experimental data on self-diffusion coefficients in binary mixtures; details on entropy scaling; numerical data of the liquid molar volume; and mutual diffusion coefficients correlated with Vignes (PDF)

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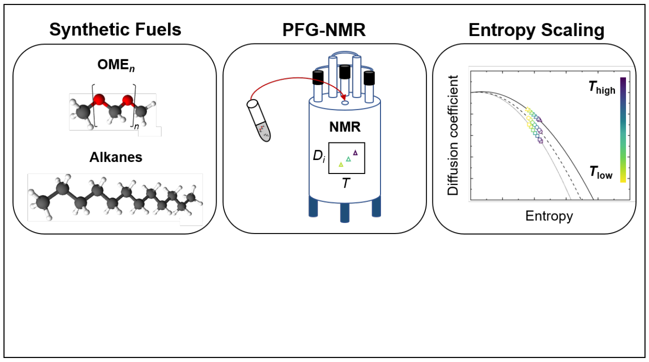
TOC Graphic


Synthetic Fuels
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n
Alkanes
PFG-NMR
NMR
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