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

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Self-diffusion coefficients of binary mixtures

The numerical experimental data for OME_n diluted in n-dodecane (C12) measured in this work are given in Table S.1. The numerical experimental data for OME_n diluted in n-hexadecane (C16) measured in this work are given in Table S.2.

Table S.1: Experimental data for the self-diffusion coefficients in binary mixtures of OME_n and n-dodecane (C12) at ambient pressure. The relative uncertainty of the experimental data of the binary mixtures is $\Delta D_1 = 0.02 \cdot 10^{-9}$ $m^2 s^{-1}$.

		OME_1/C12		OME_2/C12		OME_3/C12		OME_4/C12	
T	x_{OME_n}	D_{OME_1}	D_{C12}	D_{OME_2}	D_{C12}	D_{OME_3}	D_{C12}	D_{OME_4}	D_{C12}
K	mol mol^{-1}	$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$	
298.15	0.005	1.747	0.852	1.408	0.912	1.182	0.849	1.100	0.854
	0.010	1.706	0.867	1.382	0.863	1.178	0.853	1.107	0.852
	0.025	1.706	0.867	1.439	0.871	1.182	0.860	1.098	0.861
	0.975	3.924	2.387	2.005	1.420	1.118	0.931	0.683	0.647
	0.990	3.983	2.437	2.007	1.443	1.105	0.931	0.665	0.630
	0.995	3.999	2.469	2.006	1.429	1.100	0.927	0.659	0.644
303.15	0.005			1.507	0.946	1.290	0.934	1.213	0.939
	0.010			1.542	0.948	1.286	0.939	1.216	0.934
	0.025			1.597	0.953	1.290	0.945	1.207	0.947
	0.975			2.160	1.532	1.223	1.021	0.752	0.713
	0.990			2.167	1.560	1.207	1.017	0.737	0.699
	0.995			2.168	1.538	1.201	1.017	0.732	0.694
313.15	0.005			1.848	1.142	1.536	1.113	1.419	1.126
	0.010			1.874	1.133	1.527	1.122	1.419	1.120
	0.025			1.866	1.138	1.536	1.128	1.427	1.129
	0.975			2.494	1.775	1.447	1.212	0.913	0.866
	0.990			2.511	1.819	1.426	1.205	0.894	0.846
	0.995			2.510	1.787	1.417	1.196	0.888	0.844
323.15	0.005			2.430	1.335	1.790	1.309	1.689	1.322
	0.010			2.231	1.339	1.799	1.322	1.665	1.320
	0.025			2.229	1.344	1.790	1.329	1.678	1.329
	0.975			2.855	2.028	1.689	1.418	1.090	1.033
	0.990			2.884	2.093	1.665	1.408	1.067	1.010
	0.995			2.878	2.031	1.654	1.405	1.059	1.062
333.15	0.005			2.806	1.557	2.088	1.521	1.945	1.546
	0.010			2.563	1.561	2.092	1.540	1.971	1.530
	0.025			2.537	1.560	2.088	1.546	1.943	1.554
	0.975			3.273	2.308	1.954	1.640	1.285	1.219
	0.990			3.293	2.400	1.922	1.629	1.255	1.194
	0.995			3.273	2.310	1.906	1.632	1.248	1.185
343.15	0.005			3.017	1.850	2.460	1.786	2.272	1.825
	0.010			2.890	1.843	2.465	1.825	2.234	1.791
	0.025			2.968	1.835	2.460	1.832	2.285	1.844
	0.975			3.717	2.668	2.311	1.938	1.548	1.469
	0.990			3.854	2.824	2.226	1.912	1.501	1.425
	0.995			3.786	2.683	2.226	1.901	1.494	1.429
353.15	0.005			3.376	2.109	2.806	2.042	2.620	2.097
	0.010			3.359	2.118	2.809	2.094	2.564	2.038
	0.025			3.367	2.102	2.806	2.102	2.605	2.114
	0.975			4.156	2.978	2.637	2.214	1.798	1.704
	0.990			4.368	3.153	2.566	2.169	1.737	1.642
	0.995			4.224	2.975	2.548	2.181	1.730	1.651

Table S.2: Experimental data for the self-diffusion coefficients in binary mixtures of OME_n and n-hexadecane (C16) at ambient pressure. The relative uncertainty of the experimental data of the binary mixtures is $\Delta D_1 = 0.02 \cdot 10^{-9}$ $m^2 s^{-1}$.

		OME_1/C16		OME_2/C16		OME_3/C16		OME_4/C16	
T	x_{OME_n}	D_{OME_1}	D_{C16}	D_{OME_2}	D_{C16}	D_{OME_3}	D_{C16}	D_{OME_4}	D_{C16}
K	mol mol^{-1}	$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$		$10^{-9} \cdot m^2 s^{-1}$	
298.15	0.005	1.104	0.387	0.826	0.380	0.745	0.380	0.616	0.377
	0.010	1.041	0.381	0.889	0.393	0.739	0.380	0.616	0.380
	0.025	1.021	0.385	0.897	0.388	0.731	0.385	0.644	0.381
	0.975	3.822	1.887	1.969	1.121	0.385	0.731	0.671	0.501
	0.990	3.940	1.986	1.988	1.166	0.380	0.739	0.663	0.506
	0.995	3.979	2.017	1.994	1.166	0.380	0.745	0.660	0.494
303.15	0.005			0.948	0.431	0.817	0.428	0.691	0.427
	0.010			1.068	0.455	0.813	0.431	0.709	0.427
	0.025			0.998	0.435	0.803	0.436	0.721	0.429
	0.975			2.125	1.218	0.436	0.803	0.746	0.561
	0.990			2.141	1.253	0.431	0.813	0.736	0.561
	0.995			2.148	1.268	0.428	0.817	0.733	0.550
313.15	0.005			1.239	0.538	0.971	0.535	0.875	0.531
	0.010			1.220	0.535	0.964	0.540	0.894	0.535
	0.025			1.248	0.541	0.956	0.543	0.903	0.542
	0.975			2.456	1.413	0.543	0.956	0.907	0.683
	0.990			2.471	1.445	0.540	0.964	0.895	0.688
	0.995			2.481	1.446	0.535	0.971	0.891	0.695
323.15	0.005			1.485	0.638	1.138	0.657	1.122	0.652
	0.010			1.461	0.684	1.132	0.662	1.122	0.648
	0.025			1.483	0.660	1.123	0.666	1.093	0.659
	0.975			2.819	1.635	0.666	1.123	1.084	0.820
	0.990			2.829	1.666	0.662	1.132	1.068	0.827
	0.995			2.842	1.694	0.657	1.138	1.065	0.810
333.15	0.005			1.867	0.804	1.319	0.788	1.374	0.780
	0.010			1.855	0.826	1.314	0.797	1.349	0.778
	0.025			1.797	0.797	1.306	0.802	1.292	0.798
	0.975			3.208	1.873	0.802	1.306	1.279	0.972
	0.990			3.214	1.903	0.797	1.314	1.258	0.969
	0.995			3.232	1.927	0.788	1.319	1.256	0.992
343.15	0.005			2.257	0.957	1.583	0.958	1.578	0.943
	0.010			2.201	1.000	1.549	0.974	1.623	0.952
	0.025			2.111	0.973	1.553	0.973	1.565	0.963
	0.975			3.723	2.207	0.973	1.553	1.535	1.173
	0.990			3.680	2.191	0.974	1.549	1.509	1.178
	0.995			3.735	2.238	0.958	1.583	1.509	1.231
353.15	0.005			2.543	1.144	1.832	1.126	1.851	1.123
	0.010			2.606	1.127	1.772	1.147	1.848	1.119
	0.025			2.466	1.141	1.786	1.136	1.839	1.130
	0.975			4.197	2.517	1.136	1.786	1.777	1.364
	0.990			4.117	2.458	1.147	1.772	1.749	1.367
	0.995			4.183	2.521	1.126	1.832	1.752	1.390

Entropy scaling

The global parameters are $g_1^{(D)} = 0.6632$ and $g_2^{(D)} = 9.4714$ and were taken from Schmitt et al.[1] The fitted model parameter for the entropy scaling models of the pure solvents are given in Table S.3. The fitted model parameter for the entropy scaling models of the binary mixtures (infinite dilution self-diffusion coefficients) are given in Table S.4.

Table S.3: Parameters for the entropy scaling models of the pure solvents to be used with Eq. (8) of the main work.

property	$\alpha_{2,i}^{(D)}$	$\alpha_{3,i}^{(D)}$
$\widehat{D}^{+}_{\mathrm{OME_2}}$	0.130	-3.629
$\widehat{D}^{+}_{\mathrm{OME_3}}$	-1.932	-3.582
$\widehat{D}^{+}_{\mathrm{OME_4}}$	-1.782	-4.489
$\widehat{D}^{+}_{\mathrm{C12}}$	-2.645	-4.178
$\widehat{D}^{+}_{\mathrm{C16}}$	-2.970	-5.194

Table S.4: Parameters for the entropy scaling models of the binary mixtures (infinite dilution self-diffusion coefficients) to be used with Eq. (8) of the main work.

property	$\alpha_{2,12}^{(D)}$	$\alpha_{3,12}^{(D)}$
$\widehat{D}^{\infty,+}_{\mathrm{OME_2,C12}}$	-1.300	-4.272
$\widehat{D}^{\infty,+}_{\mathrm{OME_2,C16}}$	2.362	-6.650
$\widehat{D}^{\infty,+}_{\mathrm{OME_3,C12}}$	-2.629	-3.905
$\widehat{D}^{\infty,+}_{\mathrm{OME_3,C16}}$	-2.580	-4.684
$\widehat{D}^{\infty,+}_{\mathrm{OME_4,C12}}$	-3.536	-3.454
$\widehat{D}^{\infty,+}_{\mathrm{OME_4,C16}}$	-1.605	-5.183
$\widehat{D}^{\infty,+}_{\mathrm{C12,OME_2}}$	-0.120	-3.527
$\widehat{D}^{\infty,+}_{\mathrm{C12,OME_3}}$	-1.459	-3.716
$\widehat{D}^{\infty,+}_{\mathrm{C12,OME_4}}$	-1.530	-4.434
$\widehat{D}^{\infty,+}_{\mathrm{C16,OME_2}}$	-1.590	-2.958
$\widehat{D}^{\infty,+}_{\mathrm{C16,OME_3}}$	-1.572	-3.835
$\widehat{D}^{\infty,+}_{\mathrm{C16,OME_4}}$	-0.431	-5.103

The Figure S.1 shows the scaled self-diffusion coefficients $\widehat{D}_i^+$ of the pure components.

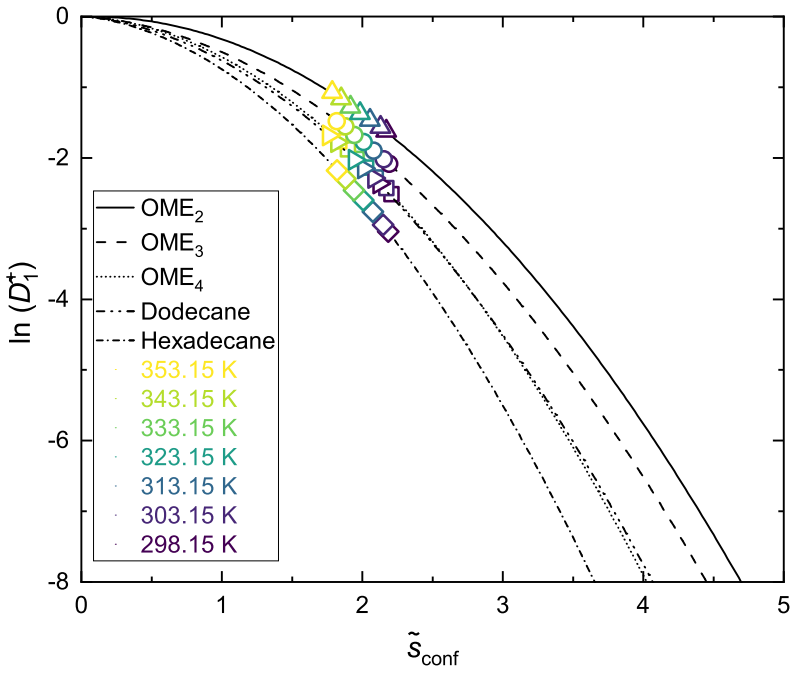

Figure S.1: Scaled self-diffusion coefficients $\widehat{D}_1^+$ of the pure components OME$_{2\text{-}4}$, n-dodecane, and n-hexadecane as function of the reduced configurational entropy $\tilde{s}$. Symbols represent the experimental results. The color of the symbols indicates the temperature. The lines are the entropy scaling fits to these data points.

In Figure S.2 and S.3, the scaled diffusion coefficients of the OME$_n$ at infinite dilution in n-dodecane (C12) and n-hexadecane (C16) are shown as function of the reduced configurational entropy $\tilde{s}$.

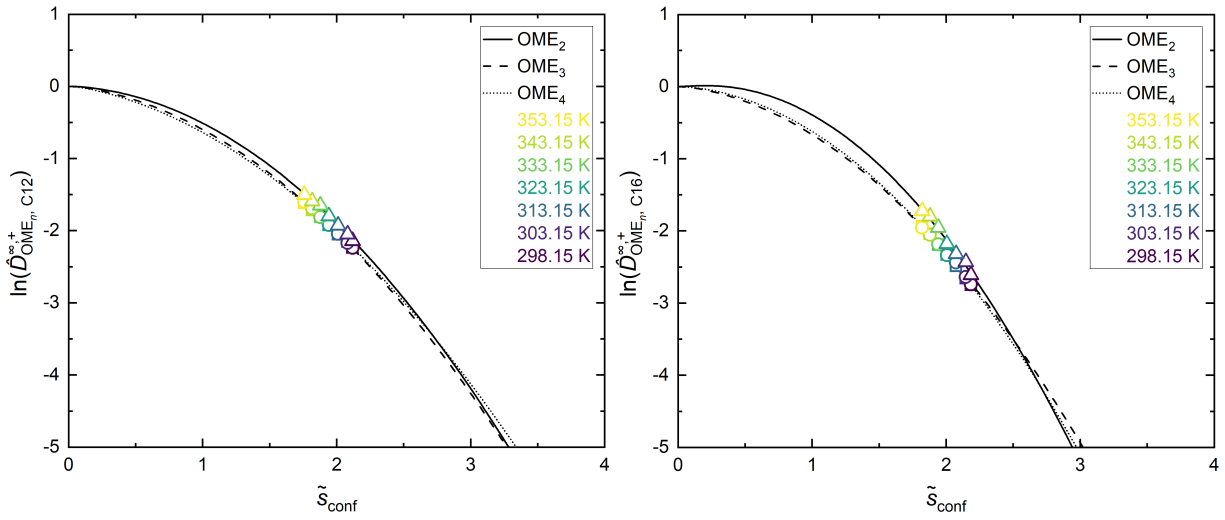

Figure S.2: Scaled diffusion coefficients of $OME_{2\text{-}4}$ at infinite dilution in *n*-dodecane $\widehat{D}^{\infty,+}_{\mathrm{OME_n,C12}}$ (left) and in *n*-hexadecane $\widehat{D}^{\infty,+}_{\mathrm{OME_n,C16}}$ (right) as function of the reduced configurational entropy $\tilde{s}$. Symbols represent the experimental results. The color of the symbols indicates the temperature. The lines are the entropy scaling fits to these data points.

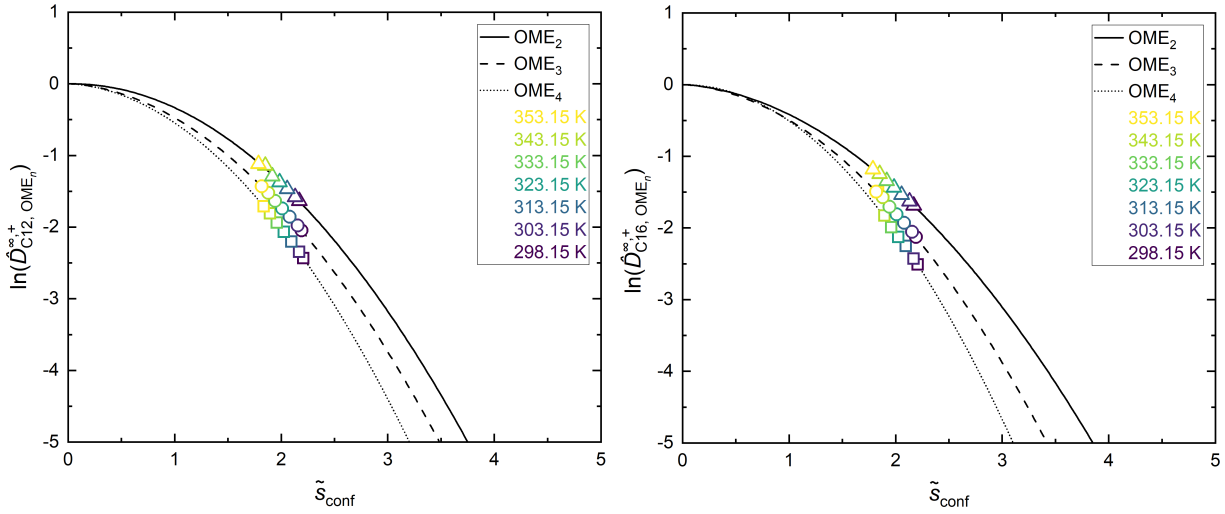

Figure S.3: Scaled diffusion coefficients of *n*-dodecane $\widehat{D}^{\infty,+}_{\mathrm{C12,OME_n}}$ (left) and *n*-hexadecane $\widehat{D}^{\infty,+}_{\mathrm{C16,OME_n}}$ (right) at infinite dilution in $OME_{2\text{-}4}$ as function of the reduced configurational entropy $\tilde{s}$. Symbols represent the experimental results. The color of the symbols indicates the temperature. The lines are the entropy scaling fits to these data points.

Liquid molar volume

Data for the liquid molar volume of the solutes at their normal boiling point v_i were obtained from Burger et al.[2] and DIPPR[3] and are listed in Table S.5.

Table S.5: Calculated data of the liquid molar volume.

i	v_i / mol cm^{-3}	T_i^s / K	Ref.
C12	$3.483 \cdot 10^{-3}$	498.35	DIPPR[3]
C16	$2.551 \cdot 10^{-3}$	560.05	DIPPR[3]
OME_2	$8.142 \cdot 10^{-3}$	378.15[4]	Burger et al.[2]
OME_3	$6.428 \cdot 10^{-3}$	429.15[4]	Burger et al.[2]
OME_4	$5.245 \cdot 10^{-3}$	474.15[4]	Burger et al.[2]

Vignes Correlation

The Figures S.4 - S.8 show the diffusion coefficients at infinite dilution obtained from NMR experiments and entropy scaling (ES) and the mutual diffusion coefficients of the binary mixtures obtained by the Vignes model for $OME_{2,3,4}$, *n*-dodecane (C12) and *n*-hexadecane (C16), respectively, for a wide temperature range. The nomenclature is the same as in the main body of the present work.

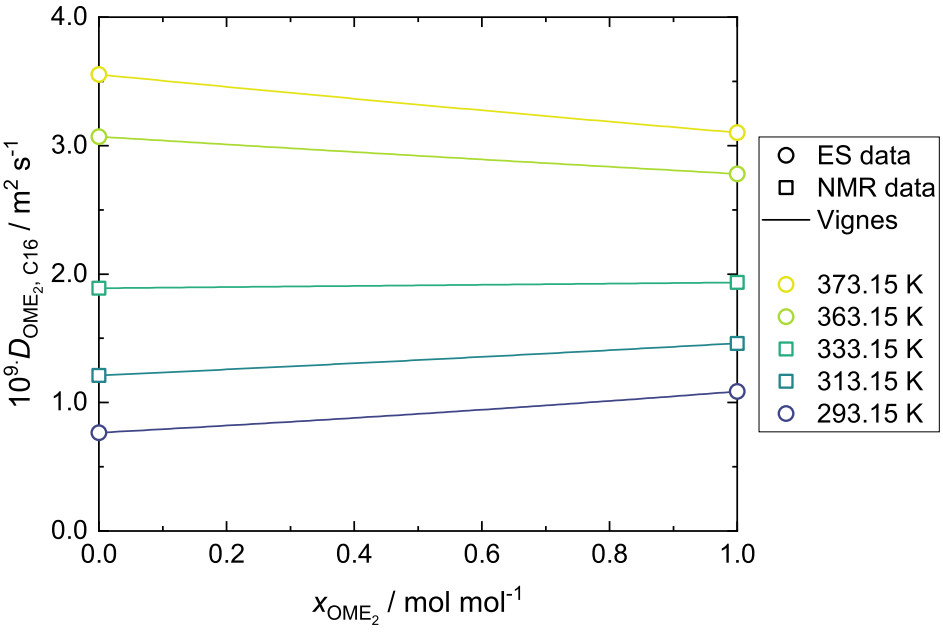

Figure S.4: Diffusion coefficients of OME_2 + n-hexadecane (C16) as a function of composition and temperature from NMR data, entropy scaling (ES) and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Lines: Vignes correlation.

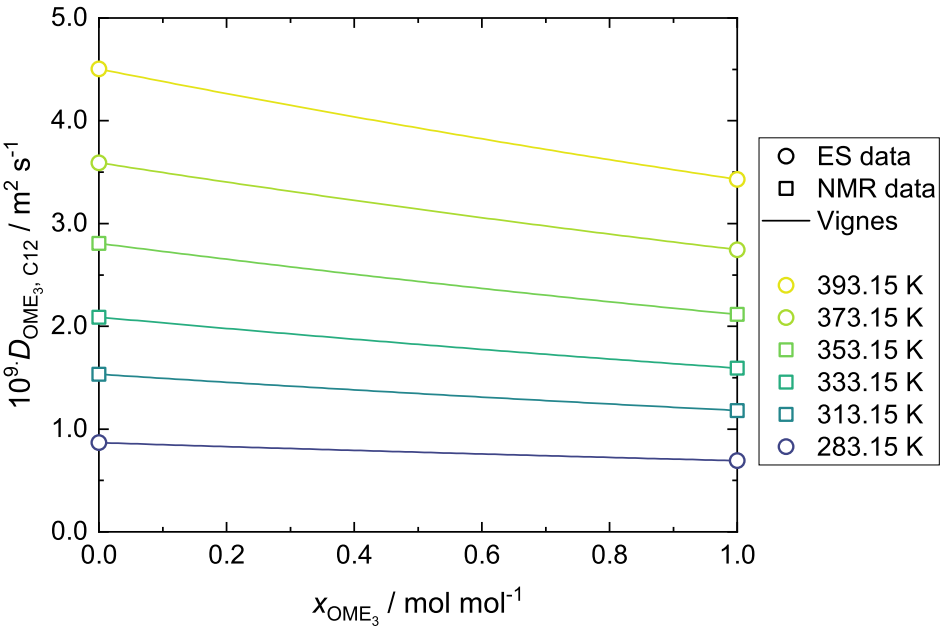

Figure S.5: Diffusion coefficients of OME_3 + n-dodecane (C12) as a function of composition and temperature from NMR data, entropy scaling (ES) and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Lines: Vignes correlation.

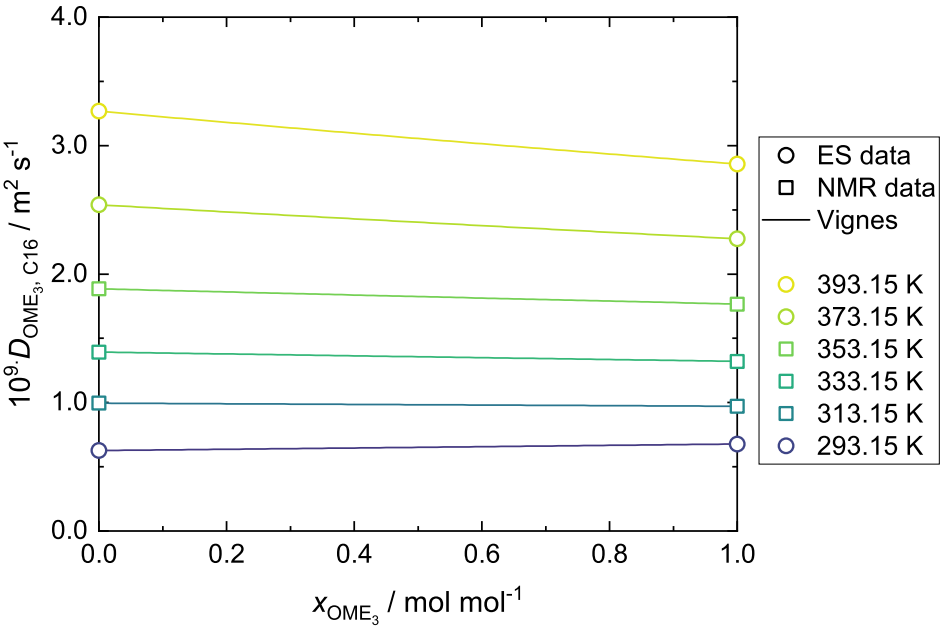

Figure S.6: Diffusion coefficients of OME_3 + n-hexadecane (C16) as a function of composition and temperature from NMR data, entropy scaling (ES) and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Lines: Vignes correlation.

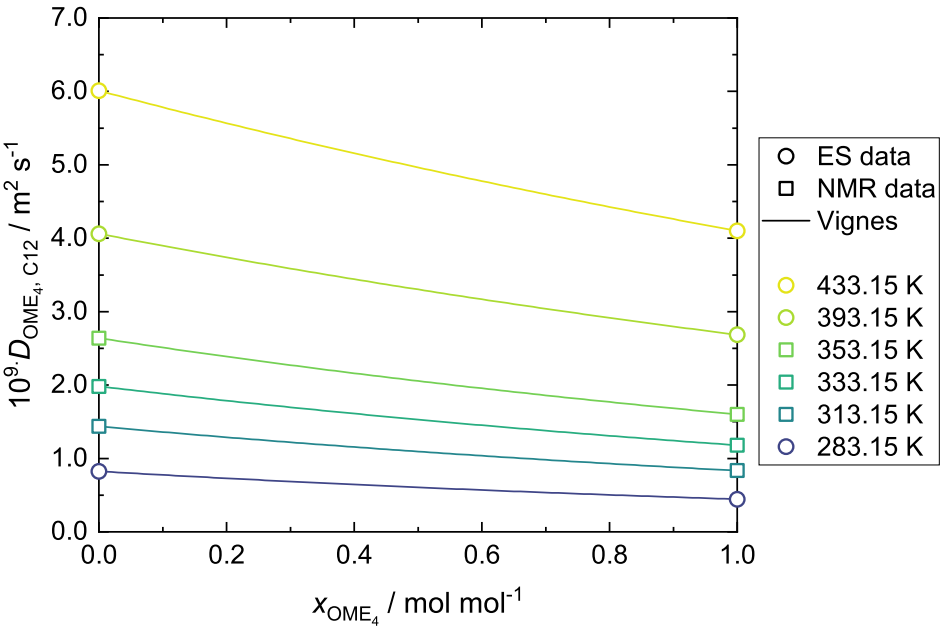

Figure S.7: Diffusion coefficients of OME_4 + n-dodecane (C12) as a function of composition and temperature from NMR data, entropy scaling (ES) and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Lines: Vignes correlation.

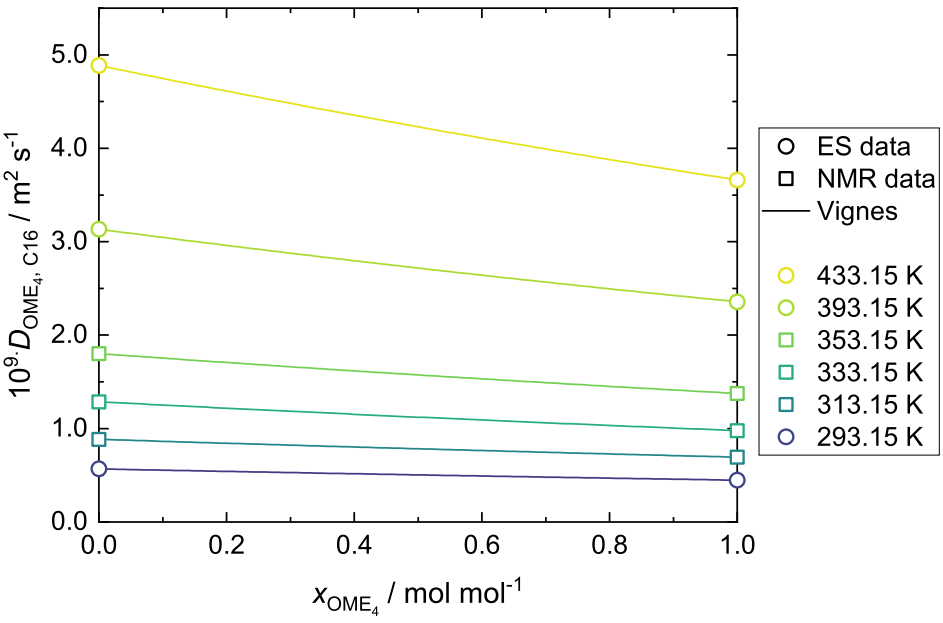

Figure S.8: Diffusion coefficients of OME_4 + n-hexadecane (C16) as a function of composition and temperature from NMR data, entropy scaling (ES) and Vignes. Symbols: NMR data (squares) and entropy scaling data (circles). Lines: Vignes correlation.

References

(1) Schmitt, S.; Hasse, H.; Stephan, S. Entropy Scaling Framework for Transport Properties using Molecular-based Equations of State. *J. Mol. Liq.* **2023**, 123811.

(2) Burger, J.; Ströfer, E.; Hasse, H. Production process for diesel fuel components poly(oxymethylene) dimethyl ethers from methane-based products by hierarchical optimization with varying model depth. *Chem. Eng. Res. Des.* **2013**, *91*, 2648–2662.

(3) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Yang, Y.; Zundel, N. A.; Daubert, T. E.; Danner, R. P. DIPPR Data Compilation of Pure Chemical Properties. Design Institute for Physical Properties, AIChE, 2003; `https://www.aiche.org/dippr`, Database date: 2018, retrieved via The DIPPR Information and Data Evaluation Manager for the Design Institute for Physical Properties - Version 12.3.0 (May 2018 Public).

(4) Burger, J.; Siegert, M.; Ströfer, E.; Hasse, H. Poly(oxymethylene) dimethyl ethers as components of tailored diesel fuel: Properties, synthesis and purification concepts. *Fuel* **2010**, *89*, 3315–3319.