Supporting Information to "Miscibility in systems containing (poly(oxymethylene) ethers (OME) + hydrocarbons + water)"

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NMR-spectroscopy

In Figure S-1 and S-2 typical ^{1}H NMR spectra of mixtures studied in the present work are shown and the peaks are assigned to components, without going into details. The individual peaks were assigned only to components and not to the exact positions of the protons in the corresponding molecules. For the evaluation, the signal of each proton was assumed to be equal of strength and that the signal is proportional to the mole fraction in the mixture. For the quantification the peak area of all protons assigned to one molecule was divided by the number of protons of this molecule and this area was set in ratio to the analogously calculated area of the other species. A detailed peak assignment of OME can be found in Schmitz et al.[1] A detailed assignment of the hydrocarbons and water can be found in [2].

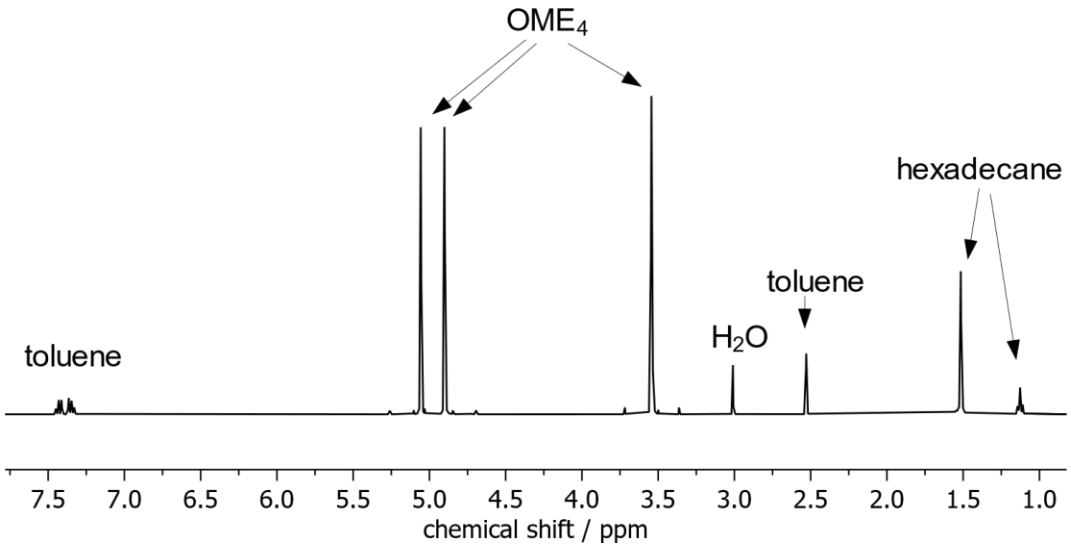

Figure S-1: ^{1}H NMR example spectrum and peak assignment for a mixture of OME_4, water, hexadecane, and toluene.

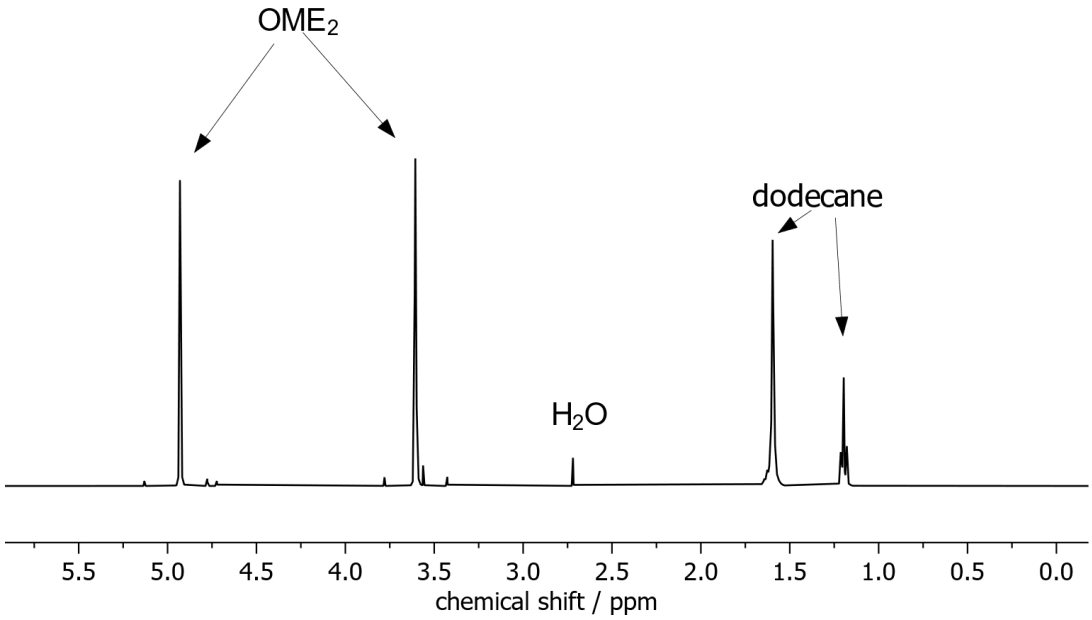

Figure S-2: ^{1}H NMR example spectrum and peak assignment for a mixture of OME_2, water, and dodecane.

Karl-Fischer titration

For the volumetric Karl-Fischer titration a automatic titrator 870 KF Tritrino plus from Metrohm was used. For the titration dry methanol (Hydranal methanol dry, Honeywell Fluka) was used as solvent and Hydranal Composite 5 (Honeywell Fluka) was as used as titrant.

For the coulometric titration a 831 KF Coulometer from Metrohm was used. A generator electrode with diaphragm was used. The cell was filled with a mixture of 0.8 g g^{-1} Hydranal-Coulomat AG-H (Honeywell Fluka) and 0.2 g g^{-1} 1-pentanol (purity >0.99 g g^{-1}, Acros Organics). The pentanol was added to achieve a homogeneous mixture between the unipolar samples and the anolyte. As katholyte in the generator electrode Hydranal Coulomat CG (Honeywell Fluka) was used.

Interaction parameters of the UNIFAC-model

The interaction parameters of the UNIFAC model were adopted from Schmitz et al. [3] where this was possible. If this was not possible, but parameters could be taken from Gmehling et al. [4], this was done. The remaining parameters were fitted to experimental data from the present work or estimated using analogies. The result is reported in Table 3 in the main test. The fitted parameters are those describing interactions between groups in OME and groups in hydrocarbons. They were fitted to data from the present work in two steps. First the toluene-free systems were considered and the corresponding parameters were fitted, without using the data for the OME-mixture. Then, the model was extended to toluene, using the experimental data for the toluene-containing systems for fitting the corresponding parameters.

The fit was carried out such that the deviations in the isoactivity criterion (cf. Equation 1 in the main text) were minimized using the Matlab software and its "lsqnonlin" routine. The target function is given in Equation S-1.

$$min \sum_{j=1}^{N_S} \begin{cases} \frac{1}{S_j} \sum_{i=1}^{N} (x_i' \cdot \gamma_i' - x_i'' \cdot \gamma_i'')^2 \, , p_j = 2 \\ \frac{1}{2 \cdot S_j} \sum_{i=1}^{N} (x_i' \cdot \gamma_i' - x_i'' \cdot \gamma_i'')^2 + (x_i' \cdot \gamma_i' - x_i''' \cdot \gamma_i''')^2 \, , p_j = 3 \end{cases} \quad \text{(S-1)}$$

Therein is N_S the number of different data sets used in the fit, S_j the number of measured equilibria measured within data set *j*, *N* the number of components, and *p* the number of phases in equilibrium in data set *j*.

Isothermal flash calculation

After calculating the starting point from the feed point the starting values for the composition of each phase was given into a minimization using the matlab function "lsqnonlin". The target function of the minimization is given in Equation S-2. The algorithm was always searching for two phases. In case of only two stable phases the composition of two phases was the same.

$$min \sum_{i=1}^{N} (x_i' \cdot \gamma_i' - x_i'' \cdot \gamma_i'')^2 + (x_i' \cdot \gamma_i' - x_i''' \cdot \gamma_i''')^2 \quad \text{(S-2)}$$

Feed compositions

In Table S-1 the composition of the feed mixtures of the measurements of this work are given.

Table S-1 Composition of the feed mixtures for the equilibrium measurements of this work. The order is the same as in Tables 5 to 10.

T / K	$x_{\mathrm{Tol}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{C12}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{C16}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{OME2}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{OME3}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{OME4}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{OME5}}^{(\mathrm{m})}$ / g g^{-1}	$x_{\mathrm{OME6}}^{(\mathrm{m})}$ / g g^{-1}
264.37	-	0.61002	-	0.32021	-	-	-	-
278.28	-	0.44988	-	0.15002	-	-	-	-
278.50	-	0.39477	-	0.39955	-	-	-	-
278.71	-	0.15071	-	0.44970	-	-	-	-
293.15	-	0.13338	-	0.66669	-	-	-	-
	-	0.15010	-	0.54996	-	-	-	-
	-	0.29991	-	0.29945	-	-	-	-
	-	0.09997	-	0.20007	-	-	-	-
	-	0.22962	-	0.40889	-	-	-	-
	-	0.43791	-	0.13202	-	-	-	-
	-	-	0.15321	0.50812	-	-	-	-
	-	-	0.1428	0.52375	-	-	-	-

Table S-1 continued

	-	-	0.20982	0.45745	-	-	-	-
	-	-	0.29509	0.37156	-	-	-	-
	-	-	0.41646	0.24970	-	-	-	-
	-	-	0.43825	0.13189	-	-	-	-
264.27	-	0.58551	-	-	-	0.33904	-	-
265.63	-	0.41104	-	-	-	0.58374	-	-
266.71	-	0.41085	-	-	-	0.58703	-	-
266.78	-	0.40988	-	-	-	0.58904	-	-
267.19	-	0.41968	-	-	-	0.57625	-	-
278.41	-	0.40133	-	-	-	0.59368	-	-
278.43	-	0.39900	-	-	-	0.59801	-	-
278.63	-	0.39547	-	-	-	0.39516	-	-
278.84	-	0.39985	-	-	-	0.59212	-	-
278.86	-	0.40011	-	-	-	0.59839	-	-
293.15	-	0.40035	-	-	-	0.39975	-	-
	-	0.39897	-	-	-	0.59802	-	-
	-	0.39800	-	-	-	0.59700	-	-
	-	0.39716	-	-	-	0.59584	-	-
	-	-	0.35015	-	-	0.39972	-	-
	-	-	0.39601	-	-	0.59399	-	-
	-	-	0.39757	-	-	0.59643	-	-
	-	-	0.39907	-	-	0.59893	-	-
		-	0.36234	-	-	0.63755	-	-
	0.00735	-	0.34315	-	-	0.39972	-	-
	0.01751	-	0.33264	-	-	0.39812	-	-
	0.07013	-	0.28012	-	-	0.40000	-	-
	-	-	0.19661	-	0.23804	0.11081	0.04515	0.01641
	-	0.19862	-	-	0.24473	0.11392	0.04641	0.01688

Modeling of the organic phase in the system (OME_n + n-alkane + water)

Figure S-3 shows the results of the modeling in the system (OME_2 + n-alkane + water) in comparison with the measured data.

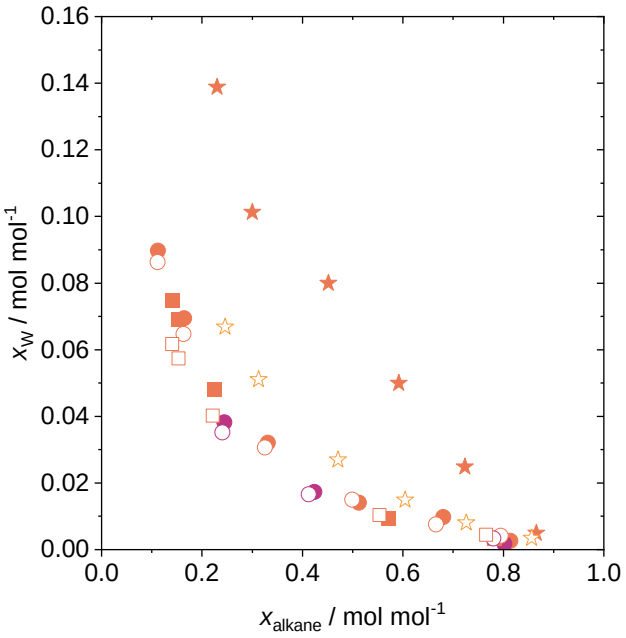

Figure S-3: Experimental results (filled symbols) and model results (open symbols) for the LLE in the system (OME_2 + C12 + water, circles) and the system (OME_2 + C16 + water, squares). The color represents the temperature: (orange) 293 K, (magenta) 278 K. Stars show the experimental results for the data of Zhuang et al.[5] for n-hexane and were modeled in this work.

Figure S-3 shows that the composition of the organic phase is well described by the model. The model was also used to simulate the experiments of Zhuang et al.[5] that were carried out with n-hexane. Interestingly, the model yields a much lower solubility of water, which is closer to the results from the present work, than that reported by Zhuang et al.[5]. This meets the expectations from the experiments of the present work, that indicate only a weak effect of the chain length of the alkane on the results.

Figure S-4 shows the results for the organic phases in the system (OME_4 + n-alkane + water)

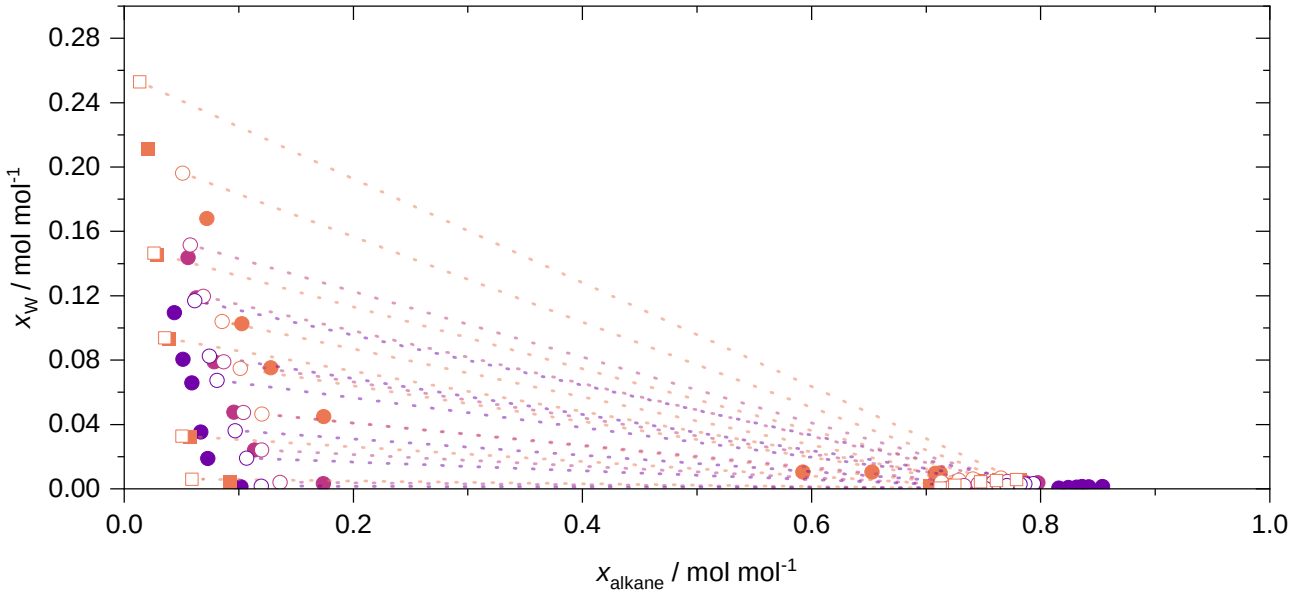

Figure S-4: Experimental results (filled symbols) and model results (open symbols) for the LLE in the system (OME_4 + C12 + water, circles) and the system (OME_4 + C16 + water, squares) at low water fractions. The color represents the temperature: (orange) 293 K, (magenta) 278 K, (purple) 265 K. Dashed lines represent tie lines of the modeled results.

The influence of the temperature on the ratio OME/n-alkane in the OME-rich phase in the two-phase area in mixtures with OME_4 (c.f. Figure 8) is systematically underestimated. For 293 K the calculated alkane concentration in the OME-rich phase is to high, for 265 K it is too low.

References

(1) Schmitz, N.; Friebel, A.; Harbou, E. von; Burger, J.; Hasse, H. *Liquid-liquid equilibrium in binary and ternary mixtures containing formaldehyde, water, methanol, methylal, and poly(oxymethylene) dimethyl ethers. Fluid Phase Equilibria* **2016**, *425*, 127–135. DOI: 10.1016/j.fluid.2016.05.017.

(2) *SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology,date of access).*

(3) Schmitz, N.; Breitkreuz, C. F.; Ströfer, E.; Burger, J.; Hasse, H. *Vapor-liquid equilibrium and distillation of mixtures containing formaldehyde and poly(oxymethylene) dimethyl ethers. Chemical Engineering and Processing: Process Intensification* **2018**, *131*, 116–124. DOI: 10.1016/j.cep.2018.06.012.

(4) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Vapor-liquid equilibriums by UNIFAC group contribution. Revision and extension. 2. Ind. Eng. Chem. Proc. Des. Dev.* **1982**, *21* (1), 118–127. DOI: 10.1021/i200016a021.

(5) Zhuang, Z.; Zhang, J.; Liu, D. *Liquid-liquid equilibria for ternary systems polyoxymethylene dimethyl ethers + water + n-hexane. CIESC Journal* **2016**, *67* (9), 3545–3551. DOI: 10.11949/j.issn.0438-1157.20160391.