

Supporting Information

Generalized Chemical Equilibrium Constant of the Formaldehyde Oligomerization

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NMR Peak Assignment

System (Formaldehyde + Water + Ethanol)

The nomenclature for the carbon nuclei of Formaldehyde oligomers is explained in Figure 2 in the main script, which also contains the ¹³C NMR spectrum. For oligomers with more than three oxymethylene groups, the assignments of carbon nuclei added by oligomerization reactions of formaldehyde is analogous to the given examples. The peak assignment of methylene glycol (MG₁) and poly(oxymethylene) glycol species (MG_{*n*}, *n* ≥ 2) is in agreement

with the chemical shift peak assignment of literature data^{1,2} and MG_n corresponding carbon peaks were assigned unambiguously by serial dilution experiments. Some oligomeric species have homotopic carbon nuclei, thus carbons (e.g. $\text{C}_{\text{MG}_2}^1$) appear twice in the structure but can not be distinguished. The chemical shifts of the carbon nuclei obtained from the ^{13}C NMR spectrum in Figure 2 in the main script are listed in Table S1.

Table S1: ^{13}C -peak assignments and chemical shifts for the system (formaldehyde + water + ethanol), sample E1, the temperature is 293 K, reference = TMS.

δ / ppm	Assignment
17.01	$\text{C}_{\text{HF}_n}^1, n \geq 2$
17.11	$\text{C}_{\text{HF}_1}^1$
19.94	$\text{C}_{\text{Ethanol}}^1$
59.81	$\text{C}_{\text{Ethanol}}^2$
65.37	$\text{C}_{\text{HF}_1}^2$
66.12	$\text{C}_{\text{HF}_2}^2$
66.34	$\text{C}_{\text{HF}_3}^2$
66.39	$\text{C}_{\text{HF}_n}^2, n \geq 4$
84.90	$\text{C}_{\text{MG}_1}^1$
87.74	$\text{C}_{\text{MG}_2}^1$
87.90	$\text{C}_{\text{HF}_2}^4$
88.35	$\text{C}_{\text{MG}_3}^1$
88.41	$\text{C}_{\text{HF}_3}^5$
88.51-88.60	$\text{C}_{\text{MG}_n}^1, n \geq 4$
90.46	$\text{C}_{\text{MG}_2}^2$
90.58	$\text{C}_{\text{HF}_3}^4$
90.86	$\text{C}_{\text{HF}_1}^3$
93.62	$\text{C}_{\text{HF}_2}^3$
94.27	$\text{C}_{\text{HF}_3}^3$
94.48	$\text{C}_{\text{HF}_n}^3, n \geq 4$

The NMR-active carbon nucleus $\text{C}_{\text{MG}_1}^1$ (peak l) of methylene glycol is separated from the rest of the peaks in the ^{13}C NMR spectrum and is located in the high-field slope (84-96 ppm) with a chemical shift of 85 ppm. The carbon nuclei of poly(oxymethylene) glycols are influenced by the number of added formaldehyde molecules. $\text{C}_{\text{MG}_2}^1$ (peak m) is shifted to 88 ppm and $\text{C}_{\text{MG}_n}^1$ ($n \geq 3$) to a range of chemical shift about 88-89 ppm. The $\text{C}_{\text{MG}_n}^n$ ($n \geq 2$) are shifted to 91 ppm, see Table S1. For the assignment of the carbon peaks of

hemiformal (HF_1) and poly(oxyethylene) hemiformals (HF_n), the peaks are fragmented into 3 different areas in the ^{13}C NMR spectrum. The low-field slope (17-20 ppm) contains peaks of methyl carbon nuclei $\text{C}_{\text{HF}_1}^1$, $\text{C}_{\text{HF}_n}^1$, and $\text{C}_{\text{Ethanol}}^1$ of the alcoholic substructure. The carbon nucleus $\text{C}_{\text{Ethanol}}^1$ (peak n) of the solvent ethanol occurs at 20 ppm. Carbon nucleus $\text{C}_{\text{HF}_1}^1$ (peak a) of HF_1 and carbon nuclei ($n \geq 2$, peak d) of HF_n -species at 17 ppm. The carbon peak $\text{C}_{\text{HF}_n}^1$ ($n \geq 2$) of long-chained poly(oxyethylene) hemiformals is influenced by the high-field shifted carbon nucleus $\text{C}_{\text{HF}_n}^2$ of the methylene group. As a consequence of the number of bridged formaldehyde molecules, a low-field shift for the carbon peaks of the methyl groups of HF_n -species ($n \geq 1$) is detected. The effect dampens with the chain length and distance to the oxygen nucleus or poly(oxyethylene) chain, so the methyl carbon nuclei of all HF_n -species ($n \geq 2$, peak d) overlap in a broadened peak at 17 ppm.

The second area contains the carbon peaks of methylene groups $\text{C}_{\text{HF}_1}^2$, $\text{C}_{\text{HF}_n}^2$, and $\text{C}_{\text{Ethanol}}^2$ of the alcoholic substructure. The carbon nucleus $\text{C}_{\text{Ethanol}}^2$ (peak o) of ethanol methylene groups is located at 60 ppm. The formed oligomers exhibit a high-field shift for carbon nuclei $\text{C}_{\text{HF}_n}^2$ ($n \geq 2$, e.g. $\text{C}_{\text{HF}_2}^2$ in peak e, $\text{C}_{\text{HF}_3}^2$ in peak h) to 66-67 ppm. A high-field shift caused by oxygen-bridged nuclei from added formaldehyde molecules is analyzed.

The third area of the spectrum, the high-field slope from 85-95 ppm, contains the carbon peaks of nuclei of the methylene groups bridged to two oxygen atoms. This area is divided into two subareas. On the right hand side of the high-field slope (84-90 ppm), NMR-active carbon nuclei with hydroxyl and oxygen-bridged methylene groups (e.g. $\text{C}_{\text{HF}_2}^4$ in peak f) are found. On the left hand side (90-95 ppm) carbon nuclei with two oxygen-bridged methylene groups (e.g. $\text{C}_{\text{HF}_2}^3$ in peak g) are found.

System (Formaldehyde + Water + 1-Propanol)

The nomenclature for the carbon nuclei of the oligomers is explained Figure S1, which also contains the ^{13}C NMR spectrum. The chemical shifts are listed in Table S2.

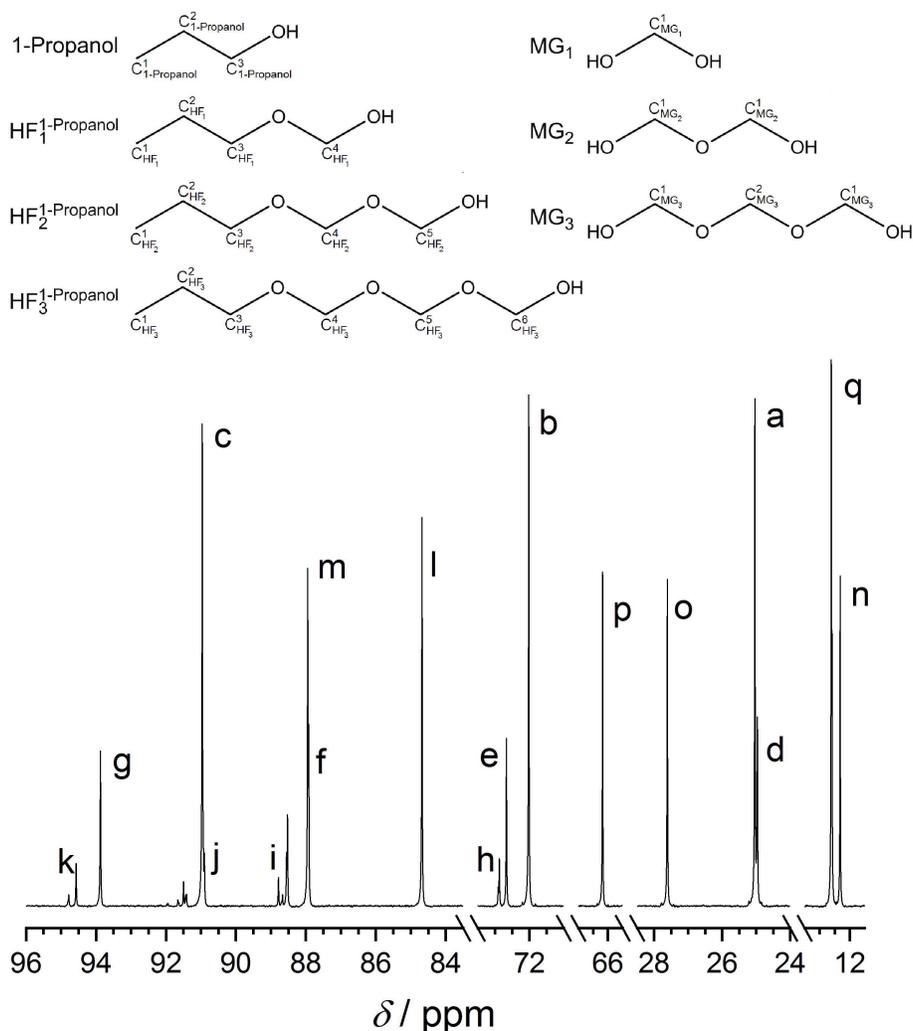


Figure S1: ¹³C NMR spectrum and peak assignments for the system (formaldehyde + water + 1-propanol), sample: P2, temperature 293 K, reference = TMSP. Assigned peaks: a = C²_{HF₁}, b = C³_{HF₁}, c = C⁴_{HF₁}, d = C²_{HF_n} ($n \geq 2$), e = C³_{HF₂}, f = C⁵_{HF₂}, g = C⁴_{HF₂}, h = C³_{HF₃}, i = C⁶_{HF₃}, j = C⁵_{HF₃}, k = C⁴_{HF₃}, l = C¹_{MG₁}, m = C¹_{MG₂}, n = C¹_{POH}, o = C²_{POH}, p = C³_{POH}, q = C¹_{HF_n} ($n \geq 1$).

The carbon NMR peaks of the different methylene glycol and poly(oxymethylene) glycol species are located at 84-91 ppm similarly to the ethanolic mixtures. In contrast to the carbon nuclei C¹_{Ethanol} and C²_{Ethanol} of the ethanol substructure, there is a second type of methylene carbon nucleus C²_{1-Propanol} in the 1-propanol substructure C¹_{1-Propanol}, C²_{1-Propanol}, and C³_{1-Propanol}. Those methylene group peaks for C²_{HF₁} (peak a) and C²_{HF_n} ($n \geq 2$, peak d) are located at 25 ppm for oligomeric species and C²_{1-Propanol} (peak o) at 28 ppm.

Table S2: ^{13}C -peak assignments and chemical shifts for the system (formaldehyde + water + 1-propanol), sample P2, the temperature is 293 K, reference = TMSP.

δ / ppm	Assignment
12.32	$\text{C}_{1\text{-Propanol}}^1$
12.59	$\text{C}_{\text{HF}_n}^1, n \geq 2$
12.62	$\text{C}_{\text{HF}_1}^1$
24.97	$\text{C}_{\text{HF}_n}^2, n \geq 2$
25.04	$\text{C}_{\text{HF}_1}^2$
27.61	$\text{C}_{1\text{-Propanol}}^2$
66.18	$\text{C}_{1\text{-Propanol}}^3$
72.02	$\text{C}_{\text{HF}_1}^3$
72.67	$\text{C}_{\text{HF}_2}^3$
72.88	$\text{C}_{\text{HF}_3}^3$
72.91	$\text{C}_{\text{HF}_n}^3, n \geq 4$
84.68	$\text{C}_{\text{MG}_1}^1$
87.92	$\text{C}_{\text{HF}_2}^5$
87.95	$\text{C}_{\text{MG}_2}^1$
88.53	$\text{C}_{\text{MG}_3}^1$
88.55	$\text{C}_{\text{HF}_3}^6$
90.90	$\text{C}_{\text{HF}_3}^5$
90.96	$\text{C}_{\text{HF}_1}^4$
93.88	$\text{C}_{\text{HF}_2}^4$
94.57	$\text{C}_{\text{HF}_3}^4$
94.78	$\text{C}_{\text{HF}_n}^4, n \geq 4$

The carbon peaks $\text{C}_{\text{HF}_n}^1$ (peak q) and $\text{C}_{1\text{-Propanol}}^1$ (peak n) of the methyl groups occur at around 12 ppm in the ^{13}C NMR spectrum. The carbon peak $\text{C}_{1\text{-Propanol}}^1$ (peak n) of 1-propanol molecules are located further right than those of poly(oxymethylene) hemiformals (e.g. $\text{C}_{\text{HF}_1}^1$, peak q). A high-field shift for the carbon nucleus $\text{C}_{\text{HF}_n}^2$ ($n \geq 2$) of the methylene group is detected. This is a result of the influenced nucleus $\text{C}_{\text{HF}_n}^3$, which is shifted to down-field regions of the spectrum. The methylene group carbon nucleus $\text{C}_{\text{HF}_1}^3$ (peak b) of the alcoholic substructure, with one oxygen-bridged methylene group, shows a peak at 72 ppm in the spectrum. The carbon nuclei $\text{C}_{\text{HF}_n}^3$ ($n \geq 2$) of long-chained oligomers are located at around 72.5 ppm, with a high-field shift. The chemical shift for this position is also explained by the number of oxygen-bridged nuclei from added formaldehyde in the oligomeric species.

Equivalent to the ethanolic mixtures, the high-field slope (84-95 ppm) of the ^{13}C NMR spectrum contains carbon nuclei with two oxygen-bridged nuclei. On the right hand side of this area, carbon nuclei (e.g. $\text{C}_{\text{HF}_3}^6$ in peak i) with a connection to a hydroxyl group and an oxygen-bridged methylene group are located. On the left side of the high-field slope (90-95 ppm), methylene carbon nuclei (e.g. $\text{C}_{\text{HF}_3}^5$, peak j) with two oxygen-bridged methylene groups are located. The assignment of the 1-propanol-based species distribution is in full agreement with the ethanol-based peak assignment.

Calculation and Modeling of Peak Area Ratios

NMR spectra were processed with the software MestReNova from Mestrelab Research S.L.. Peak area ratios ζ_i were calculated as defined in Equations (1) to (5). The variables x_i denote the mole fractions of the species i in which R stands for $-\text{CH}_2\text{CH}_3$ in the case of ethanol and $-\text{CH}_2\text{CH}_2\text{CH}_3$ in the case of 1-propanol. Quantitative information were collected solely from methylene group peaks, that do not overlap with other species. This was tested by using the non-reactive, ternary mixture of ethanol, dimethoxymethane, and 1-butanol. The relative errors of the determined mole fractions of the different components in the test mixture are less than 4% in comparison to the gravimetric sample preparation with relative errors less than 1%. This mixture contains carbon nuclei of methylene and methyl groups that are similar to those of the oligomers of ethanolic and 1-propanolic formaldehyde solutions. In Table S3, the values of the gravimetrically calculated mole fractions are compared for the three species to those mole fractions determined by ^{13}C NMR analysis. The maximum deviation is found for 1-butanol and is about 3%.

Table S3: Comparison of gravimetrically and ^{13}C NMR-determined mole fractions for a non-reactive system (ethanol + 1-butanol + dimethoxymethane), the temperature is 293 K.

Method	$x_{\text{Ethanol}} / \text{mol mol}^{-1}$	$x_{1\text{-Butanol}} / \text{mol mol}^{-1}$	$x_{\text{Dimethoxymethane}} / \text{mol mol}^{-1}$
Gravimetric	0.4786	0.2120	0.3094
NMR analysis	0.4778	0.2048	0.3173
Deviation	0.16 %	3.39 %	2.58 %

The peak area ratios are directly determined from the peak areas A that are specific for the assigned carbon nuclei of ^{13}C NMR spectra, c.f. Figure 2 in the main script and Table S4 for ethanolic samples and Figure S1 and Table S5 for 1-propanolic samples.

$$\zeta_{\text{MG}_1} = \frac{x_{\text{MG}_1}}{x_{R\text{-OH}}} = \frac{A_l}{A_o} \quad (1)$$

$$\zeta_{\text{MG}_2} = \frac{x_{\text{MG}_2}}{x_{R\text{-OH}}} = \frac{A_m}{2 \cdot A_o} \quad (2)$$

$$\zeta_{\text{HF}_1} = \frac{x_{\text{HF}_1}}{x_{R\text{-OH}}} = \frac{A_b}{A_o} \quad (3)$$

$$\zeta_{\text{HF}_2} = \frac{x_{\text{HF}_2}}{x_{R\text{-OH}}} = \frac{A_g}{A_o} \quad (4)$$

$$\zeta_{\text{HF}_3} = \frac{x_{\text{HF}_3}}{x_{R\text{-OH}}} = \frac{A_k}{A_o} \quad (5)$$

The factor 2 in Equation (2) is a consequence of $\text{C}_{\text{MG}_2}^1$ (peak m) that results from two homotopic carbon nuclei that can not be distinguished in the spectrum.

Table S4: Peak area ratios ζ_i determined from ^{13}C NMR measurements of the systems (formaldehyde + water + ethanol). Samples, see Table 2 in the main script. The definitions of the ζ_i are given in the Equations (1) to (5).

Sample	T / K	$\zeta_{\text{HF}_1}^{\text{Ethanol}}$	$\zeta_{\text{HF}_2}^{\text{Ethanol}}$	$\zeta_{\text{HF}_3}^{\text{Ethanol}}$	ζ_{MG_1}	ζ_{MG_2}
E1	293	2.26	1.05	0.41	0.31	0.17
	315	2.14	0.91	0.35	0.35	0.21
	339	1.82	0.82	0.29	0.34	0.18
E2	293	2.04	0.76	0.25	0.61	0.31
	315	1.75	0.63	0.19	0.62	0.30
	339	1.51	0.54	0.17	0.58	0.27

Table S5: Peak area ratios ζ_i determined from ^{13}C NMR measurements of the systems (formaldehyde + water + 1-propanol). Samples, see Table 2 in the main script. The definitions of the ζ_i are given in the Equations (1) to (5).

Sample	T / K	$\zeta_{\text{HF}_1}^{\text{1-Propanol}}$	$\zeta_{\text{HF}_2}^{\text{1-Propanol}}$	$\zeta_{\text{HF}_3}^{\text{1-Propanol}}$	ζ_{MG_1}	ζ_{MG_2}
P1	293	1.57	0.54	0.16	1.21	0.51
	315	1.42	0.47	0.12	1.22	1.17
	339	1.24	0.40	0.11	1.17	0.45
P2	293	2.13	0.98	0.36	0.74	0.41
	315	1.90	0.86	0.31	0.78	0.42
	339	1.69	0.76	0.28	0.75	0.40

For the calculations of the species distribution in the system (formaldehyde + water + ethanol), overall concentrations from Table 2 in the main script and correlations for the equilibrium constants from Table 3 in the main script are used. The maximum chain length of the oligomers is set to $n = 10$. The ^{13}C NMR related peak area ratios of ethanolic samples are compared to the peak area ratios calculated via the equilibrium constants in a parity plot in Figure S2. The parity plot includes dashed lines for a deviation of 10% between $\zeta_{i,\text{measured}}$ and $\zeta_{i,\text{calculated}}$. It can be seen that there is a good agreement between the peak area ratios determined by NMR analysis and the calculated peak area ratios. The deviation for the single species peak area ratios is expressed with the mean absolute percentage deviation (*MAPD*),

$$\text{MAPD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{\zeta_i^{\text{measured}} - \zeta_i^{\text{calculated}}}{\zeta_i^{\text{measured}}} \right| \cdot 100\% \quad (6)$$

where N is the number of experiments. For ethanolic samples, the overall *MAPD*-value of calculated and measured peak area ratios is 7.0%. For the oligomeric species HF_1 , HF_2 , and HF_3 , the mean deviation is 5.1%. The lowest deviation is calculated for the species HF_1 with 2% and the highest deviation for the oligomer HF_3 with 10%. For species HF_2 the deviation is 4%.

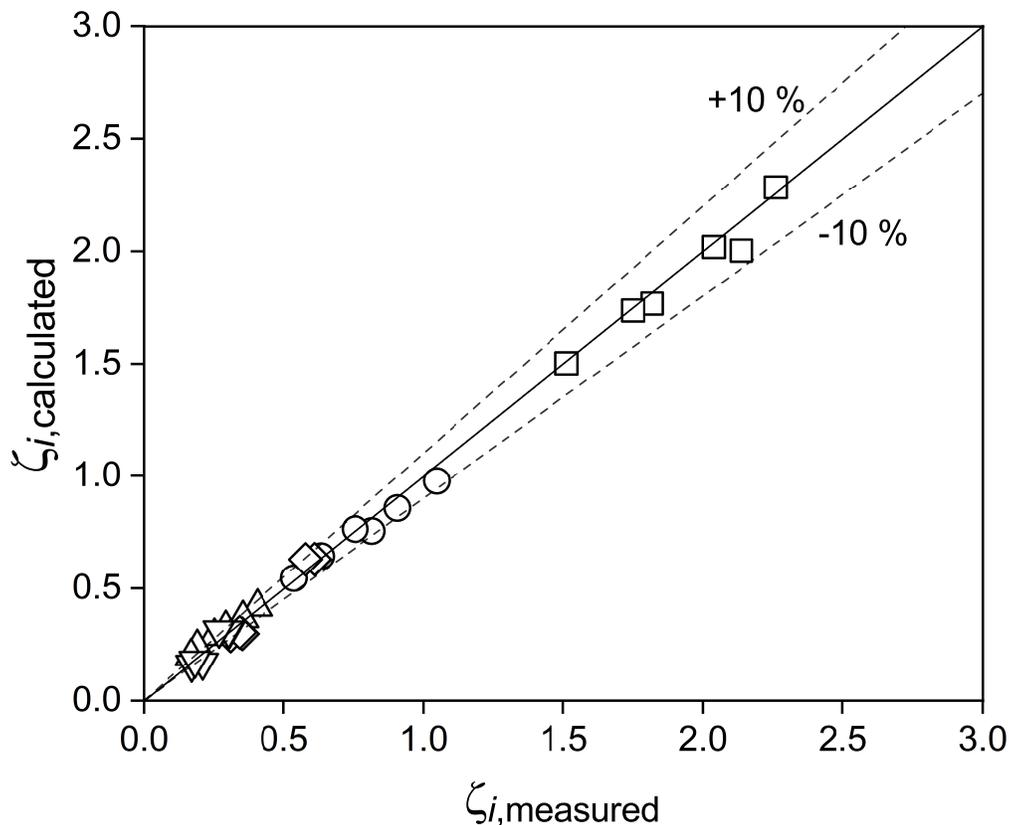


Figure S2: Parity plot showing results from the NMR-spectroscopic studies of the system (formaldehyde + water + ethanol) from the present work: comparison of measured and calculated peak area ratios (ζ_i), species (i): (\square) $\text{HF}_1^{\text{Ethanol}}$, (\circ) $\text{HF}_2^{\text{Ethanol}}$, (\triangle) $\text{HF}_3^{\text{Ethanol}}$, (∇) MG_1 , (\diamond) MG_2 .

The ^{13}C NMR related peak area ratios in the system (formaldehyde + water + 1-propanol) are compared to the peak area ratios calculated by via the equilibrium constants in a parity plot in Figure S3. In the calculations, the overall concentrations from Table 2 in the main script and correlations for the equilibrium constants from Table 3 in the main script are used. In the chemical equilibrium model calculation the maximum chain length of the oligomers is set to $n = 10$. The parity plot includes dashed lines for a deviation of 10% between $\zeta_{i,\text{measured}}$ and $\zeta_{i,\text{calculated}}$. It can be seen that there is a good agreement between the peak area ratios determined by NMR analysis and the calculated peak area ratios. For 1-propanolic samples an overall *MAPD*-value of calculated and measured peak area ratios is 6.9%. For the oligomeric species HF_1 , HF_2 , and HF_3 the mean deviation is 7.0%. The

lowest deviation is calculated for the species HF_1 with 4% and the highest value for MG_2 with 14%.

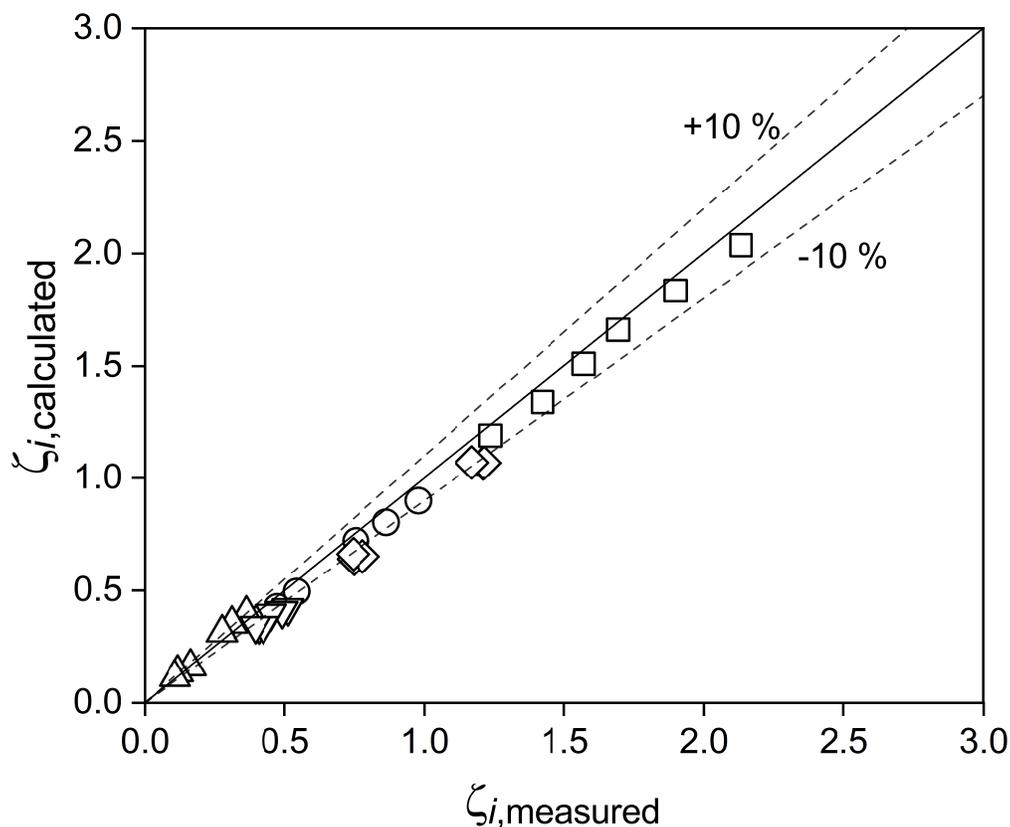


Figure S3: Parity plot showing results from the NMR-spectroscopic studies of the system (formaldehyde + water + 1-propanol) from the present work: comparison of measured and calculated peak area ratios (ζ_i), species (i): (\square) $\text{HF}_1^{1\text{-Propanol}}$, (\circ) $\text{HF}_2^{1\text{-Propanol}}$, (\triangle) $\text{HF}_3^{1\text{-Propanol}}$, (∇) MG_1 , (\diamond) MG_2 .

Remarks on the Selection of the Data Sets

The selection criteria of the data sets that were used for determining the generalized chemical equilibrium constant $K_{x,n \geq 2}$ are briefly discussed in the following. Table 1 in the main script gives an overview of all available data sets and the selected ones. For completeness, also the selection of the data that were used for the discussion of the equilibrium constant $K_{x,1}$ is briefly discussed.

Formaldehyde + Water

$n = 1$: The data from Winkelman et al.³ were used here. They report results for the chemical equilibrium constant based on measurements of adsorption kinetics and compare them to the entire previous literature, to which they fit reasonably well.

$n \geq 2$: Hahnenstein et al.¹ report chemical equilibrium constants determined with NMR spectroscopy and compare their results to the entire previous literature data. The results of Hahnenstein et al.¹ were used successfully in many subsequent studies, see e.g. Refs.^{2,4-7} Therefore, they were selected in the present study. Hahnenstein et al.¹ differentiate between $n = 2$ and $n > 2$. Their value for $n = 2$ agrees well with that of more recent studies. However, we prefer to use the value of $n > 2$, which is slightly lower, for the generalization as it can be assumed that the influence of the solvent decreases with increasing n .

Formaldehyde + Methanol

To be consistent with the results for the system (formaldehyde + water), we have also used the chemical equilibrium constant reported by Hahnenstein et al.^{1,8} for both $n = 1$ and $n > 2$. Also these data have successfully been used in many works, see above. The results for $n = 1$ reported by Hahnenstein et al. agree reasonably well with the more recent data of Gaca et al.⁹ For $n > 2$ the results can be compared with those of Balashov et al.¹⁰ and Gaca et al. The agreement with the results of Balashov et al. is very good, the results of Gaca et al. deviate from these two data sets.

Formaldehyde + Ethanol

The data from the present work was used both for $n = 1$ and $n > 2$. Besides the data from the present work, only data from Balashov et al.¹⁰ for $n > 2$ are available in the literature. These data agree very well with those from the present work.

Formaldehyde + 1-Propanol

The data from the present work are the only available source.

Formaldehyde + 1-Butanol

The data from Peschla et al.¹¹ are the only available source.

Formaldehyde + 1,4-Butynediol

The data from Berje et al.² are the only available source.

Formaldehyde + Ethylene glycol

For this system, preliminary results have been reported by Balashov et al.¹⁰. However, these authors express doubts in the accuracy of their own NMR signal assignment. They were therefore not considered in the present work.

Formaldehyde + OME

The data from Schmitz et al.⁶ are the only available source.

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