Generalized Chemical Equilibrium Constant of the Formaldehyde Oligomerization

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Abstract

Formaldehyde reacts with solvents that contain hydroxyl groups (R-OH) in oligomerization reactions to oxymethylene oligomers (R-$(\mathrm{OCH_2})_n$-OH). The chemical equilibria of these reactions have been studied in the literature for water, for the mono-alcohols methanol, ethanol, and 1-butanol, as well as for the diols ethylene glycol and 1,4-butynediol. In the present work, the collective data were analyzed. It was found that the prolongation of the oxymethylene chains by the addition of formaldehyde can be described very well with a generalized chemical equilibrium constant $K_{\mathrm{x},n\geq 2}^{R\text{-OH}}$, which is independent of the substructure (R) of the solvent. This holds for the oligomerization reactions leading to R-$(\mathrm{OCH_2})_n$-OH with $n \geq 2$. The chemical equilibrium constant $K_{\mathrm{x},1}^{R\text{-OH}}$ of the reaction of formaldehyde with the solvent R-OH depends on the solvent, but simple trends are observed. The hypotheses of the existence of a generalized chemical equilibrium constant $K_{\mathrm{x},n\geq 2}^{R\text{-OH}}$ was tested for the reactions of formaldehyde with ethanol and 1-propanol, for which neither $K_{\mathrm{x},1}^{R\text{-OH}}$ nor $K_{\mathrm{x},n}^{R\text{-OH}}$ were previously available. The corresponding equilibria were studied by ^{13}C NMR spectroscopy and the equilibrium constants were determined. A novel method was developed and used in these studies to obtain data on $K_{\mathrm{x},1}^{R\text{-OH}}$ by NMR spectroscopy, which is difficult due to the low amount of molecular formaldehyde. It was found that the generalized equilibrium constant is even valid for the acid-catalyzed formation of poly(oxymethylene) dimethyl ethers (OME).

Introduction

Formaldehyde (FA) is one of the most important chemical intermediates.[1] It reacts with solvents that contain hydroxyl groups R-OH in oligomerization reactions, which leads to very high solubilities of formaldehyde in these solutions. As pure formaldehyde tends to polymerize, formaldehyde is used in industrial processes almost exclusively in such solutions. The most common solvent for formaldehyde is water (W), but also the reactions with methanol and many other solvents R-OH are of interest.[2] Due to the oligomerization reactions of formaldehyde with R-OH, these solutions are always complex multicomponent mixtures.[3] For the poly(oxymethylene) oligomers of the type $R\text{-(OCH}_2)_n\text{-OH}$ the abbreviation Ol_n is used in the present work, where n denotes the number of CH_2O segments in the oligomer. The oligomers of formaldehyde with water are named poly(oxymethylene) glycols (MG_n), those with alcohols are named poly(oxymethylene) hemiformals (HF_n). Under acidic conditions also poly(oxymethylene) acetals $R\text{-(OCH}_2)_n\text{-O-}R$ are formed. These oligomerization reactions strongly influence the properties of the mixtures, e.g. they have to be considered for describing the vapor-liquid equilibrium.[3–10]

In the literature, information on the chemical equilibrium of mixtures of formaldehyde with water,[11–14] with the mono-alcohols methanol,[12,15,16] ethanol,[17] and 1-butanol[18,19] as well as with the diols ethylene glycol[17] and 1,4-butynediol[20] is available. In the present work, the entire set of available data on the oligomerization reactions of formaldehyde was analyzed. Moreover, the experimental basis was extended to oligomerization reactions of formaldehyde with the mono-alcohols ethanol and 1-propanol by studying the species distribution in the systems (formaldehyde + water + ethanol) and (formaldehyde + water + 1-propanol) by NMR spectroscopy, which is a well-established tool for the examination of reactive formaldehyde mixtures.[16,18,19,21–24] It may be astonishing that mixtures containing water were investigated here, when only the reactions in the system (formaldehyde + ethanol) and (formaldehyde + 1-propanol) are of interest. This is related to the difficulty in determining the equilibrium constant of reactions of monomeric formaldehyde with the alcohol by means of NMR spectroscopy. Monomeric formaldehyde is only present in very small amounts, such that its direct quantification by NMR spectroscopy is not possible. By using the competition between water and the alcohol in combination with the fact that the reactions of formaldehyde with water are well-known, this problem can be circumvented and the chemical equilibrium constant of the reaction of monomeric formaldehyde with the alcohol can be determined by NMR spectroscopy.

Chemical equilibrium constants should preferably be reported in a thermodynamically consistent manner; i.e. for liquid phase reactions, activities should be used rather than concentrations.[25,26] Nonetheless, we use mole fraction-based equilibrium constants in the present work. The mole fraction-based equilibrium constant K_x is related to the activity-based equilibrium constant K_a by:

$$K_\mathrm{a} = K_\mathrm{x} \cdot K_\gamma, \tag{1}$$

where K_γ is defined analogous to K_x, but with the corresponding activity coefficients γ. In general, both K_a and K_x depend on the temperature T, but the thermodynamic theory yields that K_a is independent from the composition, while K_x is in general composition-dependent. (The influence of pressure is neglected here).

Why have we, despite the theoretical shortcomings, nevertheless preferred to work with K_x instead of K_a? There are several reasons for this: The determination of activity coefficients, which are required for the calculation of K_a, is far from being trivial in formaldehyde-containing systems.[3,6–8,27,28] In principle, off-the-shelf group contribution methods, such as UNIFAC,[29,30] could have been applied to calculate K_γ, but it has been known for a long time that the standard methods yield poor results for formaldehyde-containing mixtures:[3] as a rule, at least some of the parameters of the group-contribution methods have to be revised to obtain a good description of thermodynamic data of formaldehyde-containing systems, see e.g. Maurer[3] for an early example, and Schmitz et al.[31,32] for recent examples.

Establishing a reliable and consistent group-contribution model for the non-ideality of all mixtures studied in the present work is a formidable task that would have exceed the scope of the present research by far. Moreover, even if such a group-contribution model have been developed for all solvents studied here, it is by no means clear that it would yield good results when used for prediction of systems that were not included in the present study.

Luckily, from a practical standpoint, and if the task is only to describe the chemical equilibria in formaldehyde-containing systems in solvents like those studied here, it is completely sufficient to use K_x; using K_a has no practical advantages: It is known that the numbers for K_x in solutions of formaldehyde in the polar and H-bonding solvents that are studied here do not depend strongly on the composition of the solution for a given solvent, see e.g. Berje et al.[20] Furthermore, Schmitz et al.[9] have recently compared modeling chemical equilibria in the system (formaldehyde + OME) with K_x and K_a. Their results for K_a, obtained from studies of solutions of different composition, even scatter more strongly than the corresponding results for K_x. We will show here, that these findings can be extended to the different solvents: We find a universal behavior using simply K_x, and cannot hope to obtain a more favorable results by using K_a. This implies that the K_γ in the studied systems do not vary strongly for the different systems, which is not unexpected as all solvents that are considered here a strongly polar and H-bonding. We do not claim that the simple findings presented here hold for solvents from other classes. Last but not least: The results for K_x can very easily be used to calculate K_a if an activity coefficient model is available.

In the present research, it was revealed that the prolongation of oxymethylene chains can be described very well with a generalized chemical equilibrium constant $K_{\mathrm{x},n}^{R\text{-OH}}$, which is independent of the solvent substructure (R). This holds for the oligomerization reactions that yield R-$(\mathrm{OCH_2})_n$-OH with $n \geq 2$. For solvents with two or multiple hydroxyl groups, however, symmetries have to be considered in the description of the chemical equilibria.

Contrary to the generalized chemical equilibrium constant $K_{\mathrm{x},n}^{R\text{-OH}}$ of the chain prolongation, the chemical equilibrium constant $K_{\mathrm{x},1}^{R\text{-OH}}$ of the first addition of formaldehyde to the solvent depends on R, but simple trends were found. Furthermore, we found that the generalized equilibrium constant of the chain prolongation in hemiformals $K_{\mathrm{x},n}^{R\text{-OH}}$ seems to be valid also for the chain prolongation in the formation of the corresponding acetals. This was shown for the poly(oxymethylene) dimethyl ethers (OME$_n$, $\mathrm{H_3C}$-$(\mathrm{OCH_2})_n$-O-$\mathrm{CH_3}$).

This paper is organized as follows: First, the chemical reaction system and the way, in which it is modeled here, are introduced. Then, the experiments that were carried out in the present work for the systems with ethanol and 1-propanol are described and the novel method for determining $K_{\mathrm{x},1}^{R\text{-OH}}$ is introduced. Finally, the results for the present work and those from the literature are analyzed and the general findings are presented, before we conclude.

We have chosen this standard organization of the paper to facilitate reading. In the actual research, the analysis of the literature came first, then came the hypothesis of the generalization, and only then, the experiments were carried out for validation.

Oligomerization Reactions of Formaldehyde

Mono-alcohols

Formaldehyde reacts with mono-alcohols R-OH in oligomerization reactions to poly(oxymethylenes) Ol_n, which are hemiformals in the case of alcohols and glycols in the case of water. These reactions take place without any catalyst.[12] By the first addition of formaldehyde, the smallest oligomer Ol_1 is formed, the corresponding chemical equilibrium constant is denoted as $K_{\mathrm{x},1}^{R\text{-OH}}$.

$$R\text{-OH} + \underbrace{\mathrm{CH_2O}}_{\mathrm{FA}} \xrightleftharpoons{K_{\mathrm{x},1}^{R\text{-OH}}} \underbrace{R\text{-OCH}_2\text{-OH}}_{\mathrm{Ol}_1} \tag{2}$$

The formation of higher poly(oxymethylene)s Ol_n ($n \geq 2$), is described by the chain prolongation with the chemical equilibrium constant $K_{\mathrm{x},n}^{R\text{-OH}}$.

$$\underbrace{R\text{-(OCH}_2)_{n-1}\text{-OH}}_{\mathrm{Ol}_{n-1}} + \underbrace{\mathrm{CH_2O}}_{\mathrm{FA}} \xrightleftharpoons{K_{\mathrm{x},n}^{R\text{-OH}}} \underbrace{R\text{-(OCH}_2)_n\text{-OH}}_{\mathrm{Ol}_n};\ n \geq 2. \tag{3}$$

The mole fraction-based chemical equilibrium constants of Reactions (2) and (3) are:

$$K_{\mathrm{x},1}^{R\text{-OH}} = \frac{x_{\mathrm{Ol}_1}}{x_{R\text{-OH}} \cdot x_{\mathrm{FA}}} \tag{4}$$

$$K_{\mathrm{x},n}^{R\text{-OH}} = \frac{x_{\mathrm{Ol}_n}}{x_{\mathrm{Ol}_{n-1}} \cdot x_{\mathrm{FA}}}\ ;\ n \geq 2 \tag{5}$$

Due to Reactions (2) and (3), the amount of monomeric formaldehyde in solutions of formaldehyde in hydroxyl group-containing solvents is always very low, since the formaldehyde is predominately bound in the oligomers.

In the present work, we distinguish between overall concentrations and true concentrations. The latter are found taking into account Reactions (2) and (3), whereas in the former, it is assumed that all reaction products are split up into formaldehyde and the solvent.

Diols

The reaction scheme presented in Equations (2) and (3) is too simplistic in cases, in which R contains additional hydroxyl groups. We discuss only the case of diols here, and denote them by HO-R'-OH. The reactions of formaldehyde with diols lead to different types of oligomers of the general structure HO-$(CH_2O)_l$-R'-$(OCH_2)_r$-OH. In the following, a short notation will be used in which a given oligomer is simply denoted by the pair of natural numbers (l r) that indicate the number of formaldehyde segments attached to the hydroxyl groups of the diol (formally: l for left and r for right). This notation does not imply that the resulting products are distinguishable, i.e. (23) may be the same molecule as (32). The formation of these oligomers can be described by the pyramidal reaction scheme presented in Figure 1a.

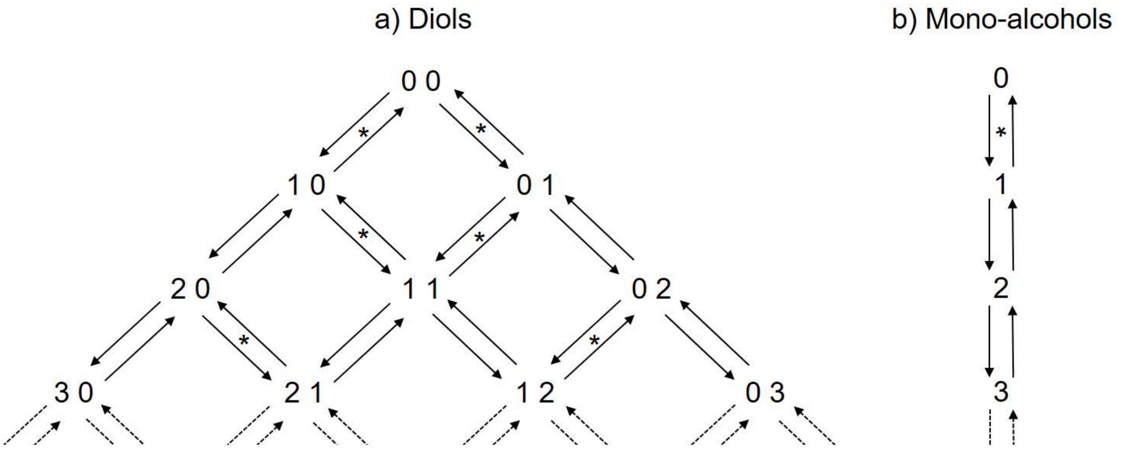

Figure 1: The panel (a) shows a reaction scheme for the formation of formaldehyde oligomers from diols. In the short notation in the figure, the oligomer HO-$(CH_2O)_l$-R'-$(OCH_2)_r$-OH is denoted by the two numbers for l and r. This notation does not imply that the resulting products are distinguishable. The arrows indicate forward and backward reactions and involve a monomeric formaldehyde molecule. For comparison, the panel (b) shows the corresponding scheme for mono-alcohols in a similar notation where the number simply stands for the number of CH_2O segments in the oligomer. The asterisk labels first addition reactions in which formaldehyde adds directly to a hydroxyl group of the diol or mono-alcohol.

The corresponding chemical equilibrium constants K_x are defined in the same way as in Equations (4) and (5), where one educt is always monomeric formaldehyde. For comparison,

Figure 1b gives the corresponding scheme for mono-alcohols. In Figure 1 reactions in which formaldehyde adds directly to R' are labeled with an asterisk. The arrows in Figure 1 indicate the forward and backward reaction, as usual.

Our hypothesis is that the values of these rate constants are the same for all reactions that are not labeled with an asterisk in Figure 1, i.e. they are not only the same for a given mono-alcohol or a given diol but also the same for all mono-alcohols and all diols and that, furthermore, there is also no difference between the mono-alcohols and diols. In contrast, the rate constants of the reactions labeled with an asterisk depend on the alcohol, but for a given diol, they are all identical.

Let us now assume that all species shown in the pyramidal reaction scheme in Figure 1a are distinguishable, i.e. that the structure of the diol is not symmetrical and the two OH-groups can be distinguished. In this case, it then follows from the above that all reactions shown in Figure 1a are distinguishable and that the equilibrium constants of all reactions that are not labeled with an asterisk in Figure 1a are identical. Also the reactions labeled with an asterisk in Figure 1a have the same equilibrium constant, which, however, generally has a different value than that of the remaining reactions.

Things get more complicated when not all species can be distinguished. The most important case is that of a symmetrical diol, in which the two hydroxyl groups cannot be discriminated, and, as a consequence, also the species $(l\ r)$ and the species $(r\ l)$ are indistinguishable. Let us consider the reaction scheme shown in Figure 1a for this case. It then contains pairs of reactions that cannot be discerned; we will call such a pair an *apparent reaction.* All distinguishable apparent reactions in the scheme shown in Figure 1a then belong to one of the following three categories:

a) two indistinguishable species are formed from one distinguishable species, e.g. (00) → (01) or (10);

b) one distinguishable species is formed from two indistinguishable species, e.g. (10) or (01) → (11);

c) two indistinguishable species are formed from two indistinguishable species, e.g. (20) or (02) → (21) or (12).

Using the same assumptions on the equality of the rate constants of the different elementary reactions that were described above leads to the following consequences for the relation between the equilibrium constant of the apparent reaction $\tilde{K}_{\mathrm{x}}$ and that of the elementary reaction K_{x} for the three categories defined above:

a) $\tilde{K}_{\mathrm{x}} = 2 \cdot K_{\mathrm{x}}$

b) $\tilde{K}_{\mathrm{x}} = 0.5 \cdot K_{\mathrm{x}}$

c) $\tilde{K}_{\mathrm{x}} = K_{\mathrm{x}}$

Water is a special case that does not fall into any of the categories discussed above. In principle, also for water, a scheme similar to the one shown in Figure 1a can be set up, as water has two locations at which formaldehyde can be added. But for water, all species that have the same number of CH_2O segments are indistinguishable, e.g. (20) = (11) = (02). The apparent reactions then have the same simple structure as that for the mono-alcohols, c.f. Figure 1b, i.e. there is only the simple chain prolongation. All apparent reactions have two pathways for the prolongation and two for the cleavage, such that for water, there is no difference between the equilibrium constant of the apparent reaction and that of the elementary reaction.

The term distinguishable is used here in a mathematical sense. As a rule, not all mathematically distinguishable species can be distinguished in an analysis of formaldehyde-containing mixtures, as the resolution of the analytical instruments is limited. The interpretation of the results of such measurements based on the reaction scheme discussed above requires an assignment of species to signals, as usual.

In the following, we report values for K_{x} and not for $\tilde{K}_{\mathrm{x}}$ for the diols as they allow a simple direct comparison with the values of mono-alcohols and water.

Literature Data

Table 1 gives an overview of the literature on the chemical equilibria of the liquid phase reactions of formaldehyde with hydroxyl group-containing solvents. Only references that report quantitative data on chemical equilibrium constants are included. For completeness, we have also added the information on the systems studied in the present work. The first addition of formaldehyde was generally studied by UV spectroscopy, as this method enables quantifying small amounts of monomeric formaldehyde. For studying the formation of higher oligomers, NMR spectroscopy is the most suitable method and has therefore been widely applied.

The amount of information on the different systems differs strongly: for the system (formaldehyde + water), plenty of data from different authors are available. Winkelman et al.[13] have given an overview of the available literature data for the first addition of formaldehyde to water, which leads to methylene glycol, and have studied this reaction themselves. The scattering of the available data is high, values of the chemical equilibrium constant $K_{\mathrm{x},1}^{\mathrm{W}}$ between 650 and 2250 at a temperature of 293 K have been reported. The formation of methylene glycol in the gas phase was studied by Hall and Piret[45] and by Kogan.[46] For the system (formaldehyde + water), plenty of information is also available on the chain prolongation reactions. Also for the system (formaldehyde + methanol), data from various authors are available. For the other systems, there is only a single source in most cases. A substantial part of the available data were measured in the laboratory of our group.

A critical comparison of the different data sets from the literature was not in the scope of the present work. For the discussions and for the establishment of the generalized correlation of the chemical equilibrium constant of the chain prolongation reaction, we use the data sets from the sources indicated by an asterisk in Table 1. The selection criteria are discussed in detail in the Supporting Information.

Table 1: Overview of the literature reporting data on chemical equilibrium constants of the reactions of formaldehyde with different solvents in the liquid phase. The data sets that were used in the present work are indicated by an asterisk (*).

Author	Year	Reactions
Formaldehyde + water		
Bieber and Trümpler[33]	1947	$n = 1$
Landqvist[34]	1955	$n = 1$
Skell and Suhr[35]	1961	$n \geq 2$
Grün and McTigue[36]	1963	$n = 1$
Ihashi et al.[37]	1965	$n \geq 2$
Siling and Akselrod[11]	1968	$n = 1$
Schecker and Schulz[38]	1969	$n = 1$
Zavitsas et al.[39]	1970	$n = 1$
Bryant and Thompson[40]	1971	$n = 1$
Koberstein et al.[41]	1971	$n \geq 2$
Sutton and Downes[42]	1972	$n = 1$
Fiala and Navrátil[43]	1974	$n \geq 2$
Slonim et al.[44]	1975	$n \geq 1$
Hahnenstein et al.*[12]	1994	$n \geq 2$
Albert et al.[6]	1999	$n \geq 1$
Winkelman et al.*[13]	2002	$n = 1$
Gaca et al.[16]	2014	$n \geq 2$
Rivlin et al.[14]	2015	$n \geq 1$
Formaldehyde + methanol		
Hahnenstein et al.*[12]	1994	$n \geq 1$
Hahnenstein et al.*[15]	1995	$n = 1$
Albert et al.[7]	2000	$n \geq 2$
Balashov et al.[17]	2002	$n \geq 2$
Gaca et al.[16]	2014	$n \geq 1$
Formaldehyde + ethanol		
Balashov et al.[17]	2002	$n \geq 2$
This work*	2020	$n \geq 1$
Formaldehyde + 1-propanol		
This work*	2020	$n \geq 1$
Formaldehyde + 1-butanol		
Peschla et al.*[18]	2003	$n \geq 2$
Formaldehyde + 1,4-butynediol		
Berje et al.*[20]	2017	$n \geq 1$
Formaldehyde + OME		
Schmitz et al.*[9]	2015	$n \geq 2$

Experimental

Chemicals, Sample Preparation, and Overall Analysis

Alcoholic formaldehyde stock mixtures were prepared by dissolving para-formaldehyde (purity ≥ 0.950 g g^{-1}, Roth) in ethanol (purity ≥ 0.999 g g^{-1}, Merck Millipore) and 1-propanol (purity ≥ 0.995 g g^{-1}, Merck Millipore), respectively, at an elevated temperature. The procedure was the same as that described by Schmitz et al.[9] The alcoholic formaldehyde stock mixtures were diluted with ultrapure water that was taken exclusively from an Elix Essential 5 purification system (Merck Millipore) to provide the samples for NMR measurements. Table 2 gives an overview of the samples that were studied. Overall mole fractions of water were determined by Karl Fischer titration,[9] overall mole fractions of formaldehyde were determined by the sodium sulfite method.[1] The relative uncertainty of both analytical results is below 2%. The overall mole fractions of the alcohols were determined as the complement to 1.0 mol mol^{-1}.

Table 2: Overall mole fractions of samples that were used for NMR measurements.

Solvent	Sample	$\tilde{x}_{\mathrm{FA}}$ / mol mol^{-1}	$\tilde{x}_{\mathrm{Alcohol}}$ / mol mol^{-1}
Ethanol	E1	0.128	0.632
	E2	0.288	0.521
1-Propanol	P1	0.220	0.501
	P2	0.277	0.611

NMR Experiments

NMR measurements were carried out with an instrument from Bruker (Ascend) with a proton resonance frequency of 400.4 MHz and a cryo probe head from Bruker (prodigy). The samples were filled in 5 mm NMR tubes from Norell and sealed after filling. Quantitative ^{13}C NMR measurements were recorded with an inverse gated decoupling pulse sequence, Nuclear Overhauser Effect (NOE) suppression was applied. The acquisition parameters for the quantitative ^{13}C NMR measurements were as follows: acquisition time 6 s, relaxation delay 90 s, flip angle 90°, and 64 scans or more. For the quantitative evaluation of the NMR spectra the same methods were applied as in previous works of our group.[9,20,23,24] These procedures ensure that the peak areas are proportional to the mole numbers of the corresponding functional groups, e.g. methylene groups in oligomeric species. Only signals from methylene groups were used for the quantitative evaluation, as they do not overlap with other signals. The uncertainty of measured mole fractions is around 3%. Details are described in the Supporting Information. Samples were equilibrated in the NMR spectrometer at the temperature of the experiment for several hours. The temperature in the NMR spectrometer was adjusted with a standard calibration method using ethylene glycol[47] and was also verified with a Pt resistance thermometer with an uncertainty of ± 0.05 K. The uncertainty of the temperature measurement in the NMR spectrometer is ± 0.5 K. The chemical shift reference in the NMR spectra is trimethyl silyl propanoic acid (TMSP). Figure 2 shows a typical ^{13}C NMR spectrum of the system (formaldehyde + water + ethanol) together with information on the peak assignment.

The corresponding information for the system (formaldehyde + water + 1-propanol) is given in the Supporting Information, where also more details on the peak assignment for both systems and a table with the corresponding chemical shifts is given.

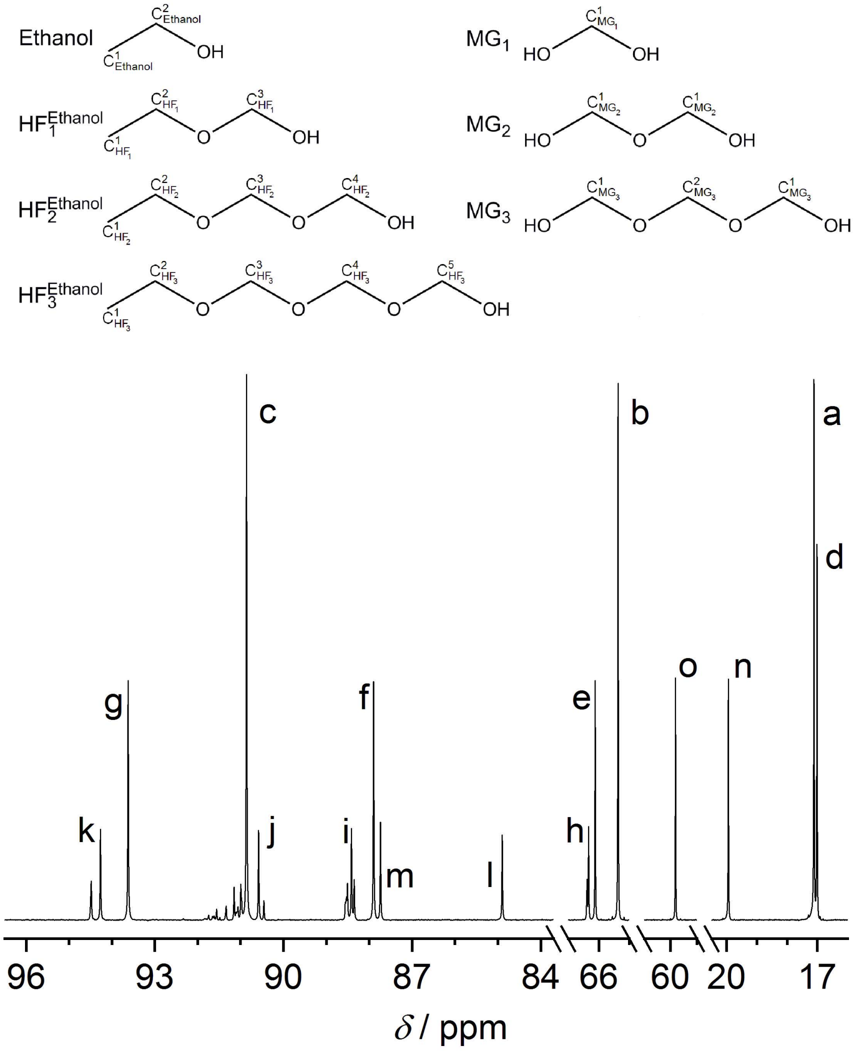

Figure 2: ^{13}C NMR spectrum and peak assignments for the system (formaldehyde + water + ethanol), sample: E1, temperature 293 K, reference = TMSP. Assigned peaks: a = $C^1_{HF_1}$, b = $C^2_{HF_1}$, c = $C^3_{HF_1}$, d = $C^1_{HF_n}$ ($n \geq 2$), e = $C^2_{HF_2}$, f = $C^4_{HF_2}$, g = $C^3_{HF_2}$, h = $C^2_{HF_3}$, i = $C^5_{HF_3}$, j = $C^4_{HF_3}$, k = $C^3_{HF_3}$, l = $C^1_{MG_1}$, m = $C^1_{MG_2}$, n = $C^1_{Ethanol}$, o = $C^2_{Ethanol}$.

Calculation of Chemical Equilibrium Constants from NMR Data

The equilibrium constants as defined in Equation (4) and (5) cannot be determined directly from the NMR data, as no information on the (very small) mole fraction of monomeric formaldehyde (CH_2O) is available. This problem can be circumvented as the studied mixtures contain not only the alcohol, which reactions with formaldehyde are of interest, but also water, which reactions with formaldehyde are well known. In principle, $K_{\mathrm{x},1}^{R\text{-OH}}$ can be obtained from $K_{\mathrm{x},1}^{\mathrm{W}}$ using the relation which follows from applying Equation (4) to water (yielding MG_1) and the mono-alcohol R-OH (yielding HF_1):

$$K_{\mathrm{x},1}^{R\text{-OH}} = K_{\mathrm{x},1}^{\mathrm{W}} \cdot \frac{x_{\mathrm{HF}_1} \cdot x_{\mathrm{W}}}{x_{R\text{-OH}} \cdot x_{\mathrm{MG}_1}}. \tag{6}$$

Rather than using Equation (6), the following relation, which can be derived in a similar manner as Equation (6), but based on Equation (5), was applied here:

$$K_{\mathrm{x},1}^{R\text{-OH}} = K_{\mathrm{x},2}^{\mathrm{W}} \cdot \frac{x_{\mathrm{HF}_1} \cdot x_{\mathrm{MG}_1}}{x_{R\text{-OH}} \cdot x_{\mathrm{MG}_2}}. \tag{7}$$

Equation (7) is preferred here for the evaluation as, first, the value of $K_{\mathrm{x},2}^{\mathrm{W}}$ is known with better accuracy than that of $K_{\mathrm{x},1}^{\mathrm{W}}$, and, secondly, as the evaluation of Equation (7) can be done solely using ^{13}C NMR data. The equilibrium constant $K_{\mathrm{x},n}^{R\text{-OH}}$ is calculated analogously to Equation (7) using the result for $K_{\mathrm{x},2}^{\mathrm{W}}$ as follows:

$$K_{\mathrm{x},n}^{R\text{-OH}} = K_{\mathrm{x},2}^{\mathrm{W}} \cdot \frac{x_{\mathrm{HF}_n} \cdot x_{\mathrm{MG}_1}}{x_{\mathrm{HF}_{n\text{-}1}} \cdot x_{\mathrm{MG}_2}} \tag{8}$$

For describing the temperature dependency of the chemical equilibrium constants, the van't Hoff equation is used:

$$\ln K_{\mathrm{x},j}(T) = A_j + \frac{B_j}{T\ /\ \mathrm{K}} \tag{9}$$

where j denotes the reaction. A_j and B_j are adjustable parameters. B_j and the reaction enthalpy $\Delta_{\mathrm{R}} h_j$ are related by the universal gas constant:

$$\Delta_{\mathrm{R}} h_j\ /\ (\mathrm{J/mol}) = -B_j \cdot 8.314\ . \tag{10}$$

The theoretical validity of Equation (10) implies that K_γ does not depend on temperature. From a practical standpoint, considering the uncertainties of the data, it can be assumed that it is valid here.

Results and Discussion

Reactions of Formaldehyde with Ethanol

The chemical equilibrium constants of the oligomerization reactions of formaldehyde with ethanol (EOH) $K_{\mathrm{x},1}^{\mathrm{EOH}}$, $K_{\mathrm{x},2}^{\mathrm{EOH}}$, and $K_{\mathrm{x},3}^{\mathrm{EOH}}$ that were obtained from the ^{13}C NMR experiments are shown in a van't Hoff plot in Figure 3. The numerical data for the peak area ratios are reported in the Supporting Information. Figure 3 shows that the differences between the results for the chemical equilibrium constants $K_{\mathrm{x},2}^{\mathrm{EOH}}$ and $K_{\mathrm{x},3}^{\mathrm{EOH}}$ are very small. Similar results have been obtained in the literature for the addition of formaldehyde to methanol,[9,15] 1-butanol[18] and 1,4-butynediol.[20] As in the literature, also in the present work the small differences between $K_{\mathrm{x},2}^{\mathrm{EOH}}$ and $K_{\mathrm{x},3}^{\mathrm{EOH}}$ were neglected and it was assumed that there is only a single chemical equilibrium constant $K_{\mathrm{x},n\geq 2}^{\mathrm{EOH}}$ that holds for all chain prolongation reactions of formaldehyde. It was obtained from a simultaneous fit to the data of $K_{\mathrm{x},2}^{\mathrm{EOH}}$ and $K_{\mathrm{x},3}^{\mathrm{EOH}}$. The van't Hoff parameters A_j and B_j for $K_{\mathrm{x},1}^{\mathrm{EOH}}$ and $K_{\mathrm{x},n}^{\mathrm{EOH}}$ are reported in Table 3, which also specifies the constant $K_{\mathrm{x},2}^{\mathrm{W}}$ used in Equations (7) and (8).

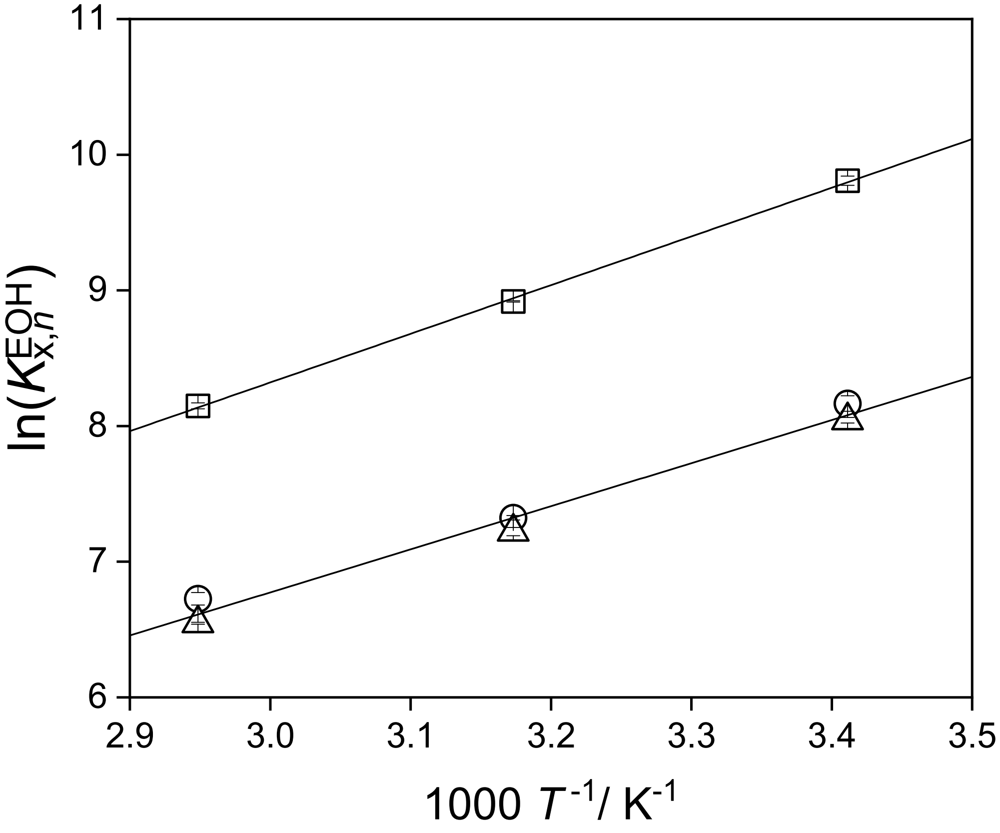

Figure 3: Van't Hoff plot for the mole fraction-based chemical equilibrium constants of formaldehyde with ethanol (EOH): (□) $K_{\mathrm{x},1}^{\mathrm{EOH}}$, (○) $K_{\mathrm{x},2}^{\mathrm{EOH}}$, (△) $K_{\mathrm{x},3}^{\mathrm{EOH}}$. The symbols are the experimental results and were obtained as arithmetic mean of the results of the study of the samples E1 and E2, see Table 2. The error bars indicate the standard deviation. Solid lines: Correlation with Equation (9) for $K_{\mathrm{x},1}^{\mathrm{EOH}}$ and $K_{\mathrm{x},n\geq 2}^{\mathrm{EOH}}$.

Table 3: Temperature-dependent correlations of chemical equilibrium constants $\ln K_n = A_j + B_j \; / \; (T/\mathrm{K})$ of formaldehyde oligomerization reactions to different solvents. Also the temperature-dependent chemical equilibrium constant of the prolongation of the acetals OME_n is given.

Solvent	n	Reference	A_j	B_j
Methanol	1	Hahnenstein et al.[15]	-1.902	3512.0
	≥ 2	Hahnenstein et al.[12]	-2.250	3008.8
Ethanol	1	This work	-2.443	3588.2
	≥ 2	This work	-2.373	3048.1
1-Propanol	1	This work	-2.246	3513.8
	≥ 2	This work	-2.311	3052.6
1-Butanol	1	Peschla et al.[18]	-1.639	3269.6
	≥ 2	Peschla et al.[18]	-1.485	2740.8
1,4-Butynediol	1	Berje et al.[20]	-2.225	3392.6
	≥ 2	Berje et al.[20]	-2.334	3032.4
Water	1	Winkelman et al.[13]	-5.494	3769.0
	2	Hahnenstein et al.[12]	-2.311	3139.9
	≥ 2	Hahnenstein et al.[12]	-2.433	3039.4
OME	≥ 2	Schmitz et al.[9]	-2.415	3029.6
General	≥ 2	This work	-2.229	2993.1

Reactions of Formaldehyde with 1-Propanol

The chemical equilibrium constants of the oligomerization reactions of formaldehyde with 1-propanol (POH) $K_{\mathrm{x},1}^{\mathrm{POH}}$, $K_{\mathrm{x},2}^{\mathrm{POH}}$, and $K_{\mathrm{x},3}^{\mathrm{POH}}$ that were obtained from the ^{13}C NMR experiments are shown in a van't Hoff plot in Figure 4. The numerical data for the peak area ratios are reported in the Supporting Information. Figure 4 shows that also for this system the differences between the results for the chemical equilibrium constants $K_{\mathrm{x},2}^{\mathrm{POH}}$ and $K_{\mathrm{x},3}^{\mathrm{POH}}$ are very small. Hence, also for this system the results were described using a single chemical equilibrium constant $K_{\mathrm{x},n\geq 2}^{\mathrm{POH}}$ that holds for all chain prolongation reactions of formaldehyde that was fitted to the results of $K_{\mathrm{x},2}^{\mathrm{POH}}$ and $K_{\mathrm{x},3}^{\mathrm{POH}}$. The van't Hoff parameters A_j and B_j for $K_{\mathrm{x},1}^{\mathrm{POH}}$ and $K_{\mathrm{x},n}^{\mathrm{POH}}$ are reported in Table 3.

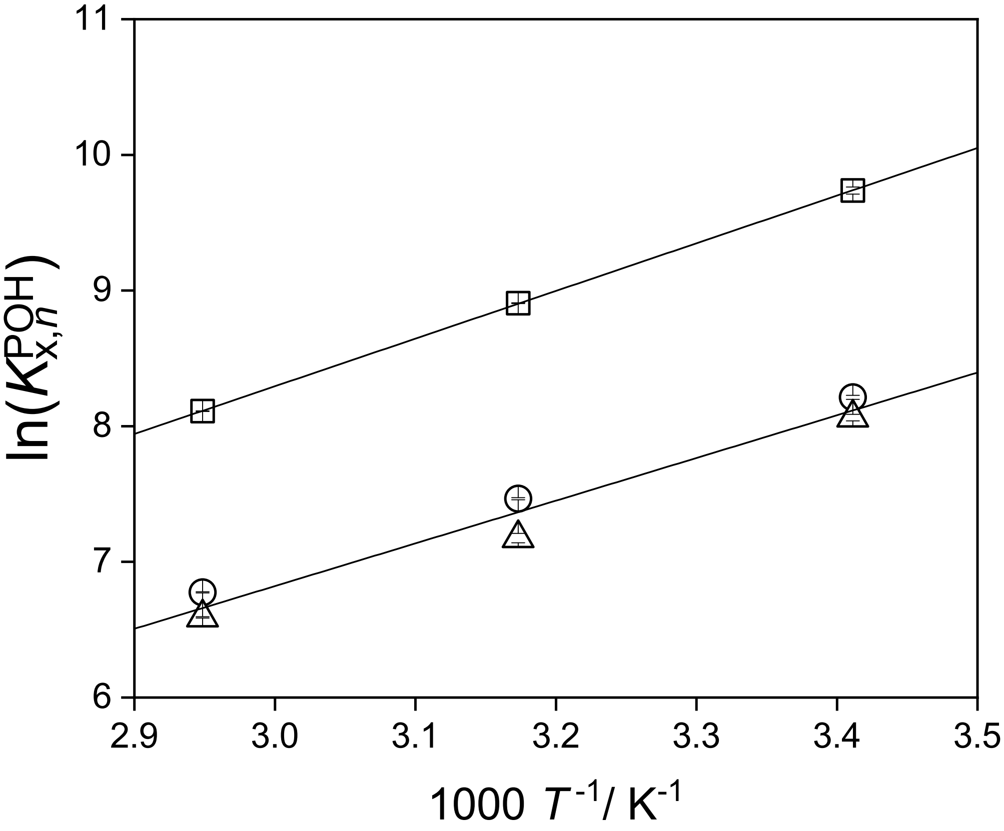

Figure 4: Van't Hoff plot for the mole fraction-based chemical equilibrium constants of formaldehyde with 1-propanol (POH): (□) $K_{x,1}^{\mathrm{POH}}$, (○) $K_{x,2}^{\mathrm{POH}}$, (△) $K_{x,3}^{\mathrm{POH}}$. The symbols are the experimental results and were obtained as arithmetic mean of the results of the study of the samples P1 and P2, see Table 2. The error bars indicate the standard deviation. Solid lines: Correlation with Equation (9) for $K_{x,1}^{\mathrm{POH}}$ and $K_{x,n\geq2}^{\mathrm{POH}}$.

Generalized Chemical Equilibrium Constant

In the following, results for the equilibrium constants of the oligomerization reactions of formaldehyde in different solvents R-OH are compared. The data sets that were considered for the present evaluation are those marked with an asterisk in Table 1. To enable a direct comparison, in many cases, the reported data had to be converted, as different ways of defining the reaction mechanism and the equilibrium constants were used by the different authors. For each of these sets, the temperature dependence of the data was correlated using the van't Hoff equation, see Equation (9). The results are presented in Table 3.

Chemical equilibrium constants of the oligomerization reactions of formaldehyde at 293 K are shown in Figure 5 for the first addition ($K_{\mathrm{x},1}^{R\text{-OH}}$) and Figure 6 for the chain prolongation ($K_{\mathrm{x},n\geq 2}$).

The chemical equilibrium constant of the first addition of formaldehyde $K_{\mathrm{x},1}^{R\text{-OH}}$ depends on the alcohol and a simple, monotonous trend is observed: the value of $K_{\mathrm{x},1}^{R\text{-OH}}$ decreases with increasing chain length of the alcohol. Also the results for the diol 1,4-butynediol fit into this trend. An even simpler result is obtained for the equilibrium constant of the chain prolongation $K_{\mathrm{x},n\geq 2}$. The numbers of $K_{\mathrm{x},n\geq 2}$ at 293 K are basically the same for all studied solvents, i.e. for all mono-alcohols, but also for water, and 1,4-butynediol. The average number and its standard deviation is 2941 ± 218. The highest deviation from the average number is observed for 1-butanol, for which also the results reported in Table 3 showed conspicuous deviations from all other data. Chan-length effects can be excluded as reason for this deviation, as the results for 1,4-butynediol fit well into the picture. The discrepancies observed for 1-butanol are attributed to the uncertainty of the underlying experimental data. This finding indicates, that the influence of R on the addition is low, once R is separated by at least one CH_2O group from the hydroxyl group, where the addition of monomeric formaldehyde takes place. This finding, although not unexpected due to chemical intuition, has, to the best of our knowledge, never been stated before.

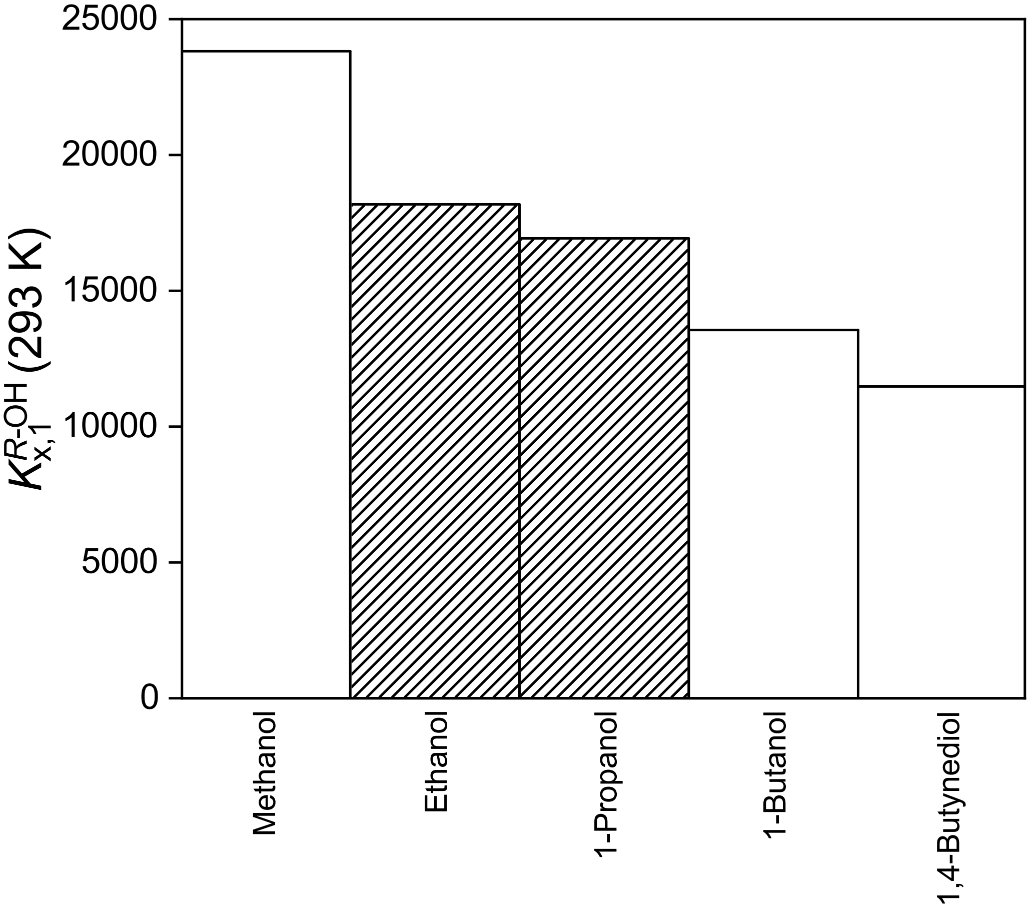

Figure 5: Values of the chemical equilibrium constants $K_{\mathrm{x},1}^{R\text{-OH}}$ of the first addition reaction of formaldehyde to: methanol,[12] ethanol and 1-propanol (this work), 1-butanol,[18] 1,4-butynediol.[20] The temperature is 293 K. The data were taken from the correlations given in Table 3. The results from the present work are hatched.

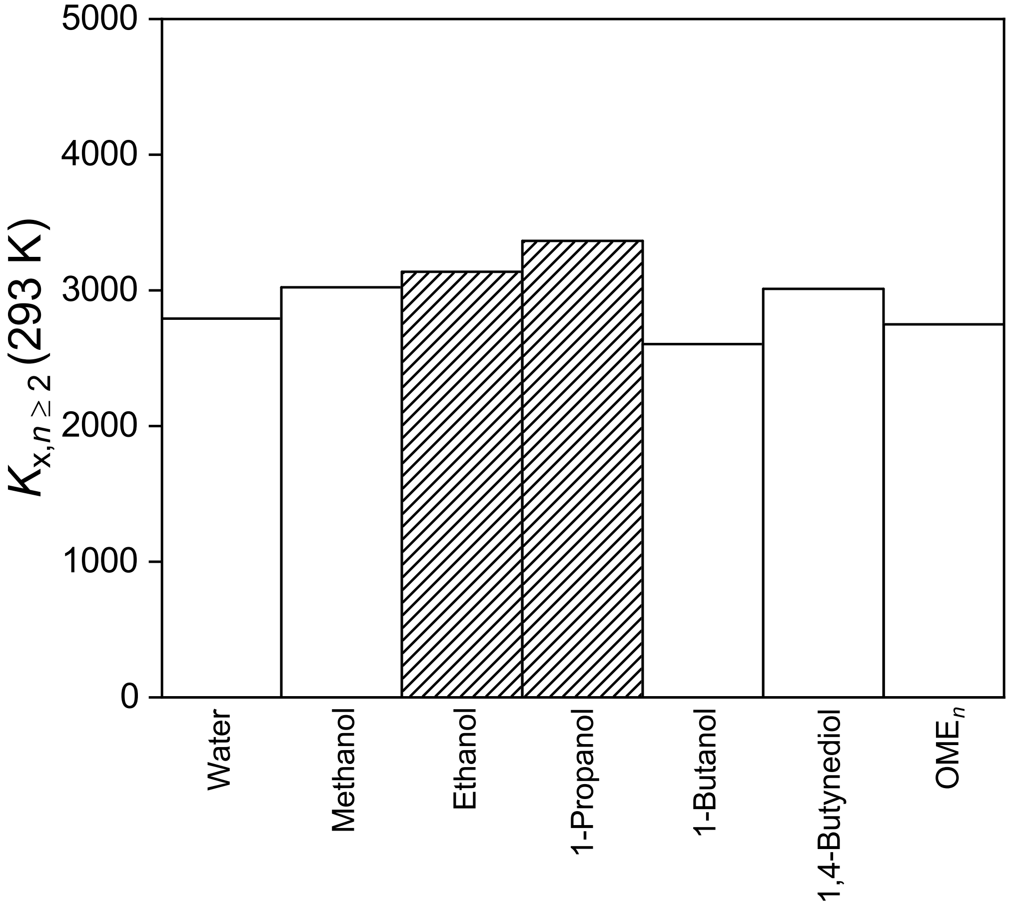

Figure 6: Values of the chemical equilibrium constants $K_{x,n}$ of the chain prolongation of formaldehyde oligomers with: water ($K^{W}_{x,n\geq 3}$),[12] methanol,[12] ethanol and 1-propanol (this work), 1-butanol,[18] 1,4-butynediol.[20] Also the chemical equilibrium constant of the prolongation of the acetals OME$_n$[9] is shown. The temperature is 293 K. The data were taken from the correlations given in Table 3. The results from the present work are hatched.

There are several ways for assessing the experimental uncertainties of the data for $K_{\mathrm{x},n\geq2}$. From an error propagation analysis of the data taken in the present work, we conclude that the relative error in the chemical equilibrium constant $K_{\mathrm{x},n\geq2}$ is at least ± 12%, even for experiments carried out with state-of-the-art equipment. For 293 K this corresponds to $K_{\mathrm{x},n\geq2} = 2941 \pm 353$. This is above the standard deviation of the results for the different solvents as shown in Figure 6, which is ± 218 and corresponds almost exactly to the maximum deviation from the mean value in Figure 6, which is observed for 1-butanol and is 325. The differences between the different results that are reported in the literature for $K_{\mathrm{x},n\geq2}$ for a given solvent (c.f. Table 1) are even larger. For the solvents water and methanol, for which enough data is available for a meaningful analysis, the results of the different authors for $K_{\mathrm{x},n=1}$ as well as $K_{\mathrm{x},n\geq2}$ at about 293 K lie in a band of about ± 600 around their mean value. Hence, it can be concluded that working with the generalized chemical equilibrium constant leads to no loss in accuracy as compared to working with the solvent-dependent numbers.

Astonishingly, also the results obtained for the chain prolongation of the poly(oxymethylene) dimethyl ethers (OME$_n$, $H_3C\text{-}(OCH_2)_n\text{-}O\text{-}CH_3$)

$$H_3C{-}(OCH_2)_{n-1}{-}O{-}CH_3 + CH_2O \xrightleftharpoons{K_{\mathrm{x},n}^{\mathrm{OME}}} H_3C{-}(OCH_2)_n{-}O{-}CH_3 \;;\; n \geq 2 \tag{11}$$

$$K_{\mathrm{x},n}^{\mathrm{OME}} = \frac{x_{\mathrm{OME}_n}}{x_{\mathrm{OME}_{n-1}} \cdot x_{\mathrm{FA}}} \tag{12}$$

fit into this rule: the number for $K_{\mathrm{x},n}^{\mathrm{OME}}$ at 293 K is basically the same as that found for the other studied oligomerization reactions of formaldehyde with water and alcohols, c.f. Figure 6. I.e. no difference was found between the uncatalyzed chain prolongation of hemiformals and that of the corresponding acetals, which requires acidic catalysis. This was only shown here for OME$_n$, i.e. for the reaction with methanol, but it may be expected that it also holds for other alcohols.

The observation made for 293 K can be generalized to other temperatures. This is shown in Figure 7, where results for the temperature dependence of the chemical equilibrium constants of the chain prolongation reactions of formaldehyde with different solvents are presented. The solvents are the same as in Figure 6. As for 293 K, the data were obtained from the correlations presented in Table 3, which were established as described above.

Again, an excellent agreement between the results for the different solvents, mono-alcohols, diols, and water, is found. The line shown in Figure 7 is the result of a correlation with the van't Hoff equation, see Equation (9), that was obtained using the entire data set. The parameters are given in Table 3. The generalized correlation represents the data well. Of course, there are some deviations between the correlations for the individual solvents and the generalized correlation, but the deviations are not larger than the typical uncertainty of the experimental determination of the equilibrium constant for an individual solvent or the deviations that are found between reliable data from different authors for a given solvent. The values of the reaction enthalpies of oligomerization reactions in different solvents, as determined from the correlations shown in Table 3 using Equation (10), lie between -21 kJ mol^{-1} and -28 kJ mol^{-1}. The oligomerization is, hence, mildly exothermal. The reaction determined from the generalized correlation is -25 kJ mol^{-1}.

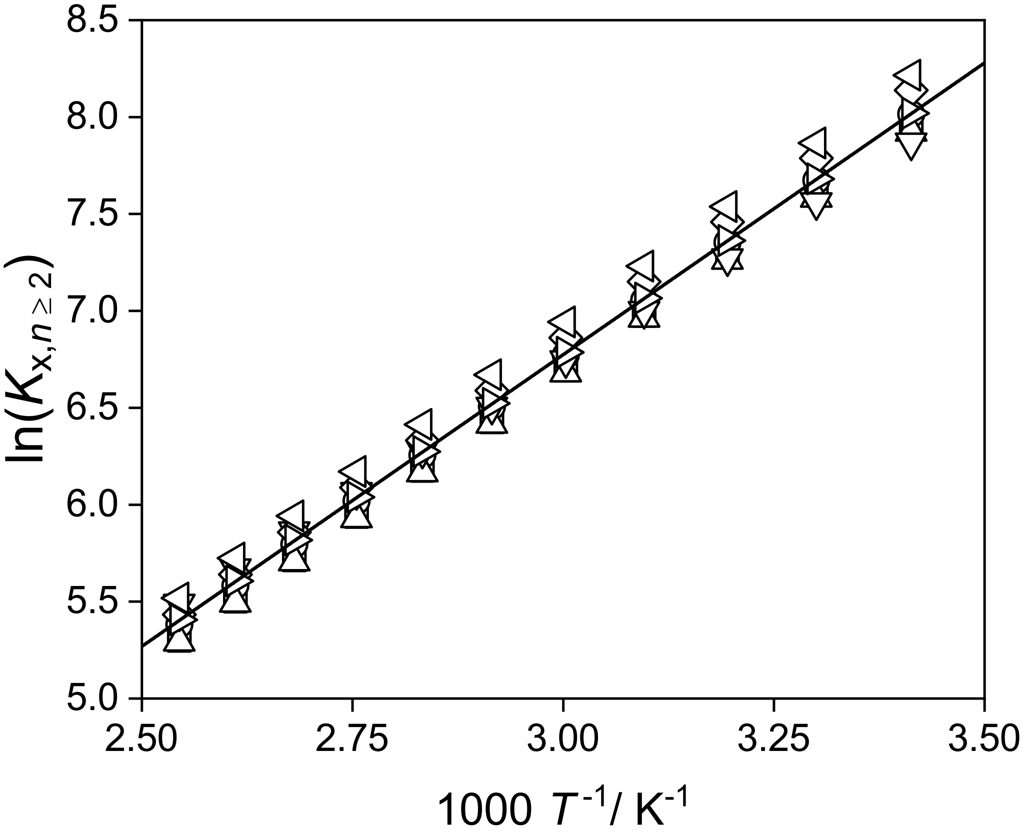

Figure 7: Van't Hoff plot for the mole fraction-based chemical equilibrium constants $K_{\mathrm{x},n\geq 2}$ of the chain prolongation reactions of formaldehyde oligomers in the following solvents: (□) water,[12] (▷) methanol,[12](◇) ethanol (this work), (◁) 1-propanol (this work), (▽) 1-butanol,[18] and (∘) 1,4-butynediol.[20] Also the chemical equilibrium constant of the prolongation of the acetals (△) OME$_n$[9] is shown. The results from the different sources were re-evaluated to bring them into a consistent form. Then, the temperature dependence was correlated using a van't Hoff equation, see Table 3. The depicted points are for fixed temperatures between 293 K and 403 K and were obtained from these correlations. Solid line: fit to the entire data set.

For completeness, Figure 8 shows the corresponding results for the temperature dependence of the first addition of formaldehyde to the different solvents that were studied here, as determined from the correlations shown in Table 3. The values of all alcohols lie in a comparatively small band in the plot shown in Figure 8. However, the differences between the different alcohols are systematic and in terms of absolute values for K_x much larger than those for the chain prolongation (compare Figure 7, but consider the different scales and absolute values). Furthermore, water is an exception here and has a distinctly lower equilibrium constant than the alcohols, which is not astonishing considering the important differences in the chemical structure. The observation made for 293 K, that the value of the chemical equilibrium constant ($K_{\mathrm{x},1}^{R\text{-OH}}$) decreases with increasing chain length of the alcohol, c.f. Figure 5, also holds for other temperatures. The values of the reaction enthalpies of the first addition reaction of formaldehyde to the different solvents, as determined from the correlations shown in Table 3 using Equation (10), lie between -27 kJ mol^{-1} and -31 kJ mol^{-1}. Hence, the first addition of formaldehyde is mildly exothermal, similar to the chain prolongation reaction.

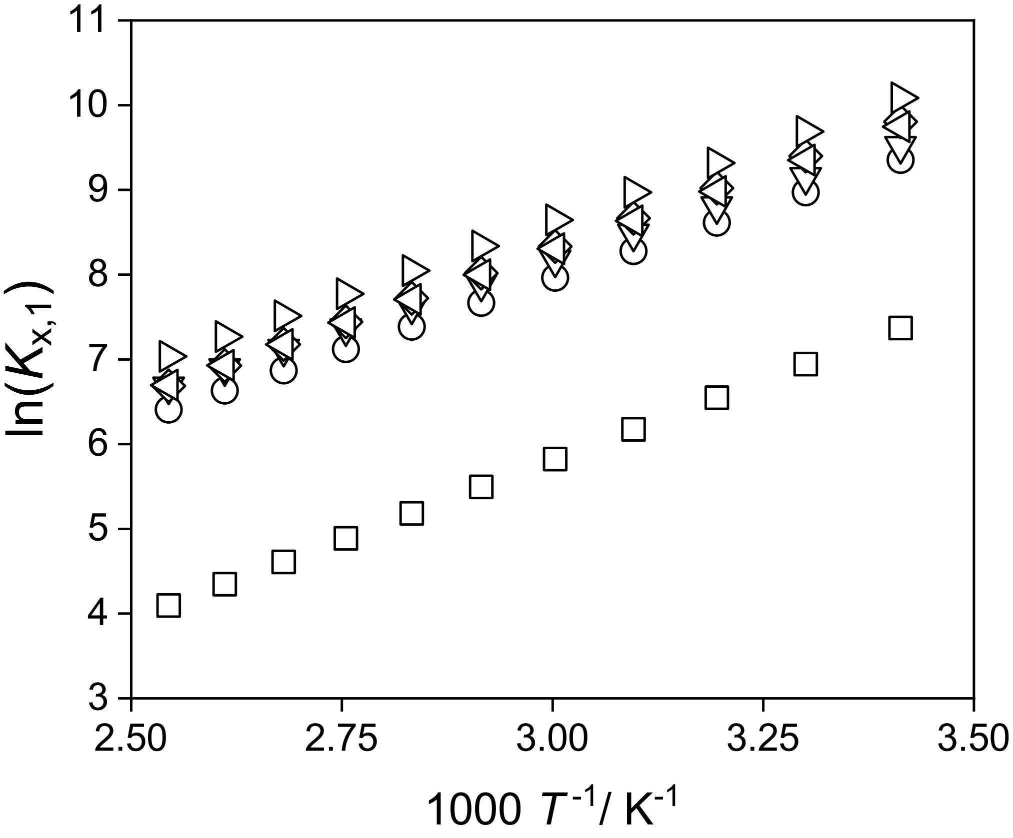

Figure 8: Van't Hoff plot for the mole fraction-based chemical equilibrium constants $K_{x,1}^{R\text{-OH}}$ of the first addition of formaldehyde to the following solvents: (□) water,[13] (▷) methanol,[12](◇) ethanol (this work), (◁) 1-propanol (this work), (▽) 1-butanol,[18] and (○) 1,4-butynediol.[20] The temperature dependence was correlated using a van't Hoff equation, see Table 3. The depicted points are for fixed temperatures between 293 K and 403 K and were obtained from these correlations.

Conclusions

Formaldehyde is one of the most important intermediates in chemical industry. It is also found in many chemical processes as a side component. The design and optimization of processes that contain formaldehyde is challenging, as formaldehyde is highly reactive. In particular, formaldehyde reacts with all substances that contain hydroxyl groups. These reactions cannot be suppressed and take place even at mild conditions and in the absence of catalyst. It is therefore important to know the chemical equilibrium constants of these reactions. Hereby usually two cases are distinguished: the first addition of formaldehyde to a substance of the type R-OH, which leads to R-OCH$_2$-OH, and the further additions leading to the oligomers of the type R-$(OCH_2)_n$-OH, which lead to the establishment of an oligomer species distribution. The equilibrium constant of the first addition is large, such that only small amounts of monomeric formaldehyde are found in solutions, even when they contain large overall amounts of formaldehyde. These reactions can be studied by UV- and NMR-spectroscopy, but corresponding quantitative experiments are tedious and have only been carried out so far for the reactions of formaldehyde with water as well as with a few alcohols. In the present work, the entire available data on these reactions was analyzed, and simple regularities were revealed. The chemical equilibrium constants of the chain prolongation leading to R-$(OCH_2)_n$-OH with $n \geq 2$ are the same for all hydroxyl group-containing substances. I.e. the addition of formaldehyde is independent of the rest R as long as the reacting hydroxyl group is separated from R by at least one CH_2O group. An universal equilibrium constant for this reaction is reported here for the first time. In contrast to the equilibrium constant of the chain prolongation, the equilibrium constant of the first addition of formaldehyde to R-OH depends on the rest R. But also here, a simple trend is observed for different alcohols: the equilibrium constant decreases as the chain length of the alcohol increases. This enables also estimating this equilibrium constant for alcohols that have not been studied yet. These results are important for the design and optimization of many processes in the chemical industry, as the behavior of formaldehyde in the processes can now be assessed more reliably without having to carry out experimental work on the chemical equilibria, when such data is unavailable in the literature.

The present work is only concerned with chemical equilibria. It is an open question whether similar generalizations as for the equilibria can also be established for reaction kinetics. Work on this is challenging as the kinetics of the reactions, that were studied here, are known to depend strongly on the pH-value. Hence, generalizing kinetics in these systems will have to involve information on the pH-value in varying non-aqueous solvents, or it would have to be limited to systems that include, besides formaldehyde and the solvent R-OH, always also water.

A further achievement of the present work is the development of a new method that enables studying the equilibrium constant of the first addition of formaldehyde to hydroxyl group-containing substances *R*-OH by NMR spectroscopy. NMR spectroscopy is regularly used for studying the chain prolongation, but could not be applied before for studying the first addition, as the concentrations of monomeric formaldehyde are so low that a reliable quantification by NMR spectroscopy is not possible. The new method circumvents this problem by studying the ternary system (formaldehyde + *R*-OH + water) and using the abundant reliable information on the equilibria in the system (formaldehyde + water). It was applied here to the systems (formaldehyde + ethanol + water) and (formaldehyde + 1-propanol + water) for which not only the equilibrium constants of the first addition of formaldehyde to the alcohol but also those of the chain prolongation reactions were determined, which were previously unknown. The results confirm the generalized findings that were revealed in the present study.

Acknowledgement

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Supporting Information Available

^{13}C NMR spectrum of the system (formaldehyde + water + 1-propanol), ^{13}C NMR peak assignment of the system (formaldehyde + water + ethanol) and system (formaldehyde + water + 1-propanol), calculation and modeling of peak area ratios of the system (formaldehyde + water + ethanol) and system (formaldehyde + water + 1-propanol), remarks on the selection of the data sets that were used for determining the generalized chemical equilibrium constant.

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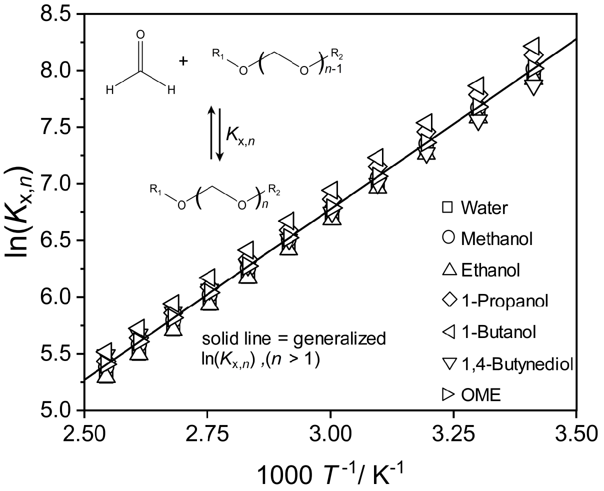

Figure 9: For Table of Contents use only. Raphael Kircher, Niklas Schmitz, Jürgen Berje, Werner R. Thiel, Jakob Burger, Hans Hasse: Generalized Chemical Equilibrium Constant of the Formaldehyde Oligomerization.