

Solubility of formaldehyde in mixtures of water + methanol + poly(oxymethylene) dimethyl ethers

Christian F. Breitkreuz^a, Jakob Burger^b, Hans Hasse^{a,}*

^aLaboratory of Engineering Thermodynamics (LTD), Technische Universität Kaiserslautern (TUK), Erwin-Schrödinger-Str. 44, 67663 Kaiserslautern, Germany; ^bLaboratory of Chemical Process Engineering, Campus Straubing for Biotechnology and Sustainability, Technical University of Munich (TUM), Uferstr. 53, 94315 Straubing, Germany

*Corresponding author, Email address: hans.hasse@mv.uni-kl.de

Abstract

Poly(oxymethylene)dimethyl ethers (OME) are a highly interesting group of oxygenates that could be used in the future as a sustainable and clean alternative to fossil diesel. Processes to produce them from formaldehyde and methanol have been developed. One remaining problem that may occur in these processes is the formation of a formaldehyde-rich solid, which has to be avoided. Nothing is known about the conditions under which this solid is formed. This gap of knowledge is closed in the present work. Based on previous fundamental work of our group on the solid-liquid equilibrium (SLE) in the system (formaldehyde + water + methanol), we have

experimentally studied the SLE in the systems (formaldehyde + water + OME) and (formaldehyde + water + methanol + OME) at temperatures between 273 K and 303 K, for two distinct species: OME₂ and OME₄. The solid phase consisted basically of pure oligomeric formaldehyde. The system (formaldehyde + water + OME) shows a complex phase behavior due to the superposition of liquid-liquid equilibria (LLE) and SLE, resulting in a solid-liquid-liquid equilibrium (SLLE). As in our previous work, the formation of the solid was described with a physico-chemical model, which considers the reactions between formaldehyde, water, and methanol. Both the equilibrium and the slow kinetics of the process are described well by the model.

Keywords: solid-liquid equilibrium, solid formation kinetics, formaldehyde, water, methanol, poly(oxymethylene) dimethyl ether, experiment, physico-chemical model, solid-liquid equilibrium

1. Introduction

Poly(oxymethylene) dimethyl ethers ($\text{CH}_3\text{-O-(CHO)}_n\text{-CH}_3$, OME) are promising sustainable and clean synthetic fuels and suited for replacing fossil diesel fuel [1–5]. Schmitz et al. [6] have developed an efficient production process for OME from aqueous formaldehyde solutions and methanol, which was recently been operated successfully in a pilot plant [7].

A ubiquitous problem in processes with formaldehyde solutions is that under certain conditions formaldehyde-rich solids may be formed [8]. These solids are long-chain formaldehyde $(\text{CH}_2\text{O})_n$, usually capped by hydroxyl terminal groups, i.e., they can be considered as paraformaldehyde. Their exact chain length is difficult to determine and in general unknown. This is highly undesired

as it leads to fouling and clogging of the equipment. The prediction of the conditions under which these solids are formed is a difficult problem. Counter-strategies had to be devised basically only relying on empirical knowledge of the given process. This has changed only recently with a report of our group on an experimental and modeling study on the formation of solids in mixtures of (formaldehyde + water + methanol), in which both the solid-liquid equilibrium (SLE) and the kinetics of the solid formation were studied [8]. Here, we extend this work to solutions that contain also OME to enable the prediction of the solid precipitation in mixtures of formaldehyde, water, methanol, and OME, as they occur in the production process of OME.

There are several reasons why predicting the solid formation from formaldehyde solutions is so difficult. Firstly, these solutions are chemically reactive, as formaldehyde reversibly forms oligomers with water and alcohols [9–11]. Furthermore, the precipitating species are long-chain oligomers that are present only in very small amounts, which results in very slow kinetics of the process. It may take hundreds of days to attain the SLE, even in the presence of catalysts that speed up the reactions [8]. This is also why most of the SLE data on formaldehyde solutions from the literature [9,12,13] overestimate the solubility of formaldehyde by far [8]. We also refer the reader to [8] for the phase diagram of the mixture (formaldehyde + water) (Figure 6 in that publication) and note only that throughout the present work, we refer only to the branch of the liquidus curve for which the solid is formaldehyde-rich and not to that for which formaldehyde-free solvent precipitates.

Furthermore, we note that one of the important findings from [8] is that precipitating species from mixtures of (formaldehyde + water + methanol) are oligomers of formaldehyde and water (and not oligomers of formaldehyde and methanol, even at high methanol concentrations. Also the experiments of the present work were carried out at conditions where this is the case.

In the present study, we have used the experimental methods from our recent work [8] to measure the solubility of formaldehyde in the systems (formaldehyde + water + OME) and (formaldehyde + water + methanol + OME). It took up to 100 days to reach equilibrium. To investigate the influence of the chain length of the OME, the studies were carried out with OME₂ and OME₄.¹ As mixtures of (formaldehyde + water + OME) show a liquid-liquid miscibility gap [14], we have also studied the solid-liquid-liquid equilibrium (SLLE). Finally, the measured data were modeled based on the physico-chemical model of [8]. This includes the modeling of the equilibrium and the kinetics of the solid formation.



2. Chemical Reactions

Formaldehyde forms oligomers with water and methanol in reversible reactions [9,10,15–17]. With water (W), formaldehyde (FA) forms poly(oxymethylene)glycols (HO-(CH₂O)_n-H, MG_n) (cf. Reactions I and II). Analogously, with methanol (MeOH), poly(oxymethylene) hemiformals (HO-(CH₂O)_n-CH₃, HF_n) are formed (cf. Reactions III and IV).



¹ We use the abbreviation OME when referring to OME in general, whereas we use the abbreviation OME_n when referring to an individual member of this class of oxygenates, with *n* CH₂O-units.

As these reactions take place also in the absence of catalysts, aqueous and methanolic formaldehyde solutions are always reactive multicomponent mixtures. The reactions (I) – (IV) can be catalyzed both by acids and bases [18,19]. In the present work, small amounts of sodium hydroxide were added to speed up the reaction kinetics.

OME can be formed from formaldehyde and methanol in the presence of strong acidic catalysts [20–22], which, however, was not the case in the experiments of the present work, so that the OME can be considered as inert components throughout this work.

Furthermore, different side reactions can occur in aqueous and methanolic formaldehyde solutions [9,15,23], namely the Cannizzaro reaction by which formic acid is formed [8,9,15,24]. These side reactions are, however, not important for the present study.

We distinguish the overall and true composition of a formaldehyde solution. The true composition is obtained considering the reactions (I) – (IV), the overall composition is obtained when formally splitting up all oligomers in formaldehyde, water, and methanol. Overall concentrations are denoted using a tilde.

3. Experiments

3.1 Chemicals

Table 1: Provenance and purity of the pure components.

chemical name / abbreviation	source	initial fraction purity	purification method	final purity	analysis method
formaldehyde ^a , FA	Carl Roth	$\geq 0.95 \text{ g g}^{-1}$	none	$\geq 0.95 \text{ g g}^{-1}$	stated by supplier
water, W	Stadtwerke Kaisers- lautern	not available	ion-exchange and filtration	$>0.99999 \text{ g g}^{-1}$	conductometry
methanol, MeOH	Sigma- Aldrich	$\geq 0.998 \text{ g g}^{-1}$	none	$\geq 0.998 \text{ g g}^{-1}$	stated by supplier
OME ₂ ^b	BASF SE	$> 0.985 \text{ g g}^{-1}$	none	$> 0.985 \text{ g g}^{-1}$	gas chromatography
OME ₄ ^c	BASF SE	$> 0.985 \text{ g g}^{-1}$	none	$> 0.985 \text{ g g}^{-1}$	gas chromatography
sodium hydroxide solution, NaOH	Fluka Analytical	3,09 mol/L	none	3,09 mol/L	stated by supplier

^a obtained in a solid polymeric form (paraformaldehyde) ^b methoxy(methoxymethoxy)methane

^c 2,4,6,8,10-pentaoxaundecane

Formaldehyde solutions were prepared by dissolving paraformaldehyde in water or methanol at elevated temperatures. The water was obtained from a Milli-Q system from Merck Millipore (specific resistance $> 15 \text{ M}\Omega \text{ cm}^{-1}$). The procedure for the preparation of the formaldehyde mixtures was the same as described by Schmitz et al. [20] in more detail. The samples for the solubility measurement were prepared by mixing the aqueous or methanolic formaldehyde stock solutions with OME₂ or OME₄. The pH values of the samples were adjusted by adding small

amounts of sodium hydroxide solution. The samples had a weight of about 40 g and were filled into 50 mL centrifuge tubes.

3.2 Studies of the formation of solids

The experimental method for studying the formation of solids in mixtures containing formaldehyde was adopted from our previous work [8]. Homogenous formaldehyde solutions were prepared as described above and the pH value was adjusted to about pH = 11. The solutions were then inserted into a thermostatted bath. The temperature of the bath was chosen such that the solution was over-saturated at this temperature and measured with a calibrated platinum resistance thermometer with an accuracy of ± 0.1 K. After a few hours, the samples turned cloudy as the solid phase started to form. At different time intervals, the samples were removed from the bath, centrifuged at the temperature of the liquid bath, and a part of the clear liquid phase (approx. 0.8 g) was removed with a syringe equipped with a syringe attachment filter (PTFE-membrane, 0.2 μ m pore diameter) and analyzed. In some experiments, a second liquid OME-rich phase was observed, like it is already known from Schmitz et al. [14] That phase, was, however, so small that it could not be analyzed, so that the analytical results always only refer to the larger of the two liquid phases. The occurrence of a second liquid phase was, however, documented. The experiments were ended when a stationary state regarding the formaldehyde concentration in the liquid phase was reached. We assume that equilibrium is then established. The criterion that was applied was that in subsequent analyses of the samples the change in the formaldehyde mass fraction was below

$2 \cdot 10^{-5} \text{ g g}^{-1} \text{ day}^{-1}$. Depending on the conditions, reaching equilibrium took between 50 and 100 days. All measurements were done at 0.1 MPa.

3.3 Chemical analysis

The analytical methods were mainly adopted from the previous work [8]. The formaldehyde concentration was measured using the sodium sulfite method with a relative uncertainty below 1% and the water concentration using Karl-Fischer titration with a relative uncertainty below 2%. The concentration of the OME was determined by gas chromatography as described by Schmitz et al. [20] with an uncertainty of 0.004 g g^{-1} .

Additionally, in some of the samples also the concentration of formic acid was determined by ion chromatography using the method from [8]. It never exceeded 0.003 g g^{-1} and was generally found to be well below that value so the formic acid is neglected in the following.

In mixtures of (formaldehyde + water + OME) the overall mass fractions of formaldehyde and OME were measured, and the overall mass fraction of water was determined by difference to 1, as the mass fractions of formaldehyde and OME were known. In mixtures of (formaldehyde + water + methanol + OME), the overall mass fractions of formaldehyde, water, and OME were measured, and the overall mass fraction of methanol was again determined by difference to 1.

4. Kinetic and equilibrium model of solid formation

For the modeling of the solid-liquid equilibrium and the kinetics of the formation of the formaldehyde-rich solid, the model described in [8] was used. It was extended here for the presence of a second liquid phase. A scheme of this physico-chemical model with the different phases is shown in Figure 1.

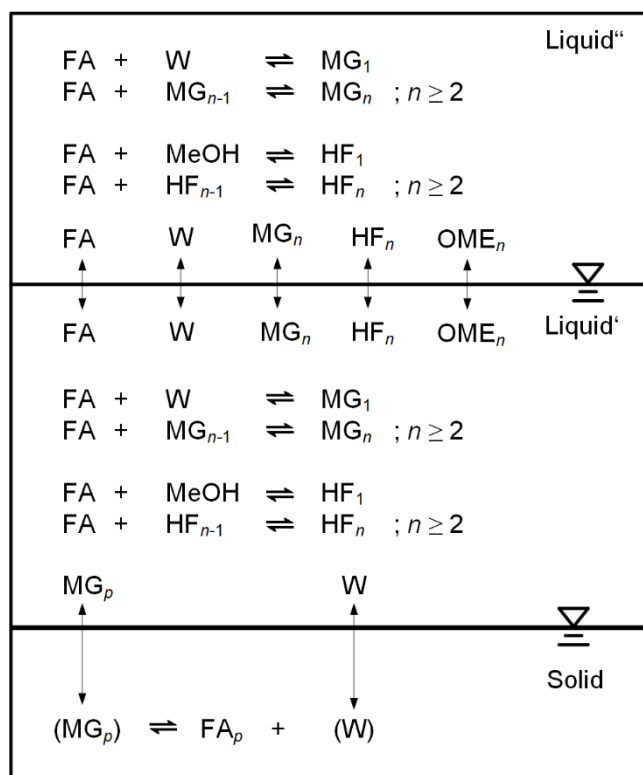


Figure 1: Scheme of the physico-chemical model of the solid-liquid-liquid equilibrium in the system (formaldehyde + water + methanol + OME_n). The symbols are explained in the text.

Since the model has already been presented in detail, it is only described briefly here. The main idea is that in formaldehyde solutions containing water and methanol (except for very high methanol concentrations, which are not considered here) upon reaching the solubility limit, the solubility constant of one particular methylene glycol MG_p (with the chain length p) is reached, so

that it is this MG_p that precipitates. In the solid phase, the MG_p polymerizes, whereby water is released to the liquid phase. In the model, we assume that pure polymeric formaldehyde (FA_p) is formed, i.e., we neglect the end groups. The degree of polymerization is not important for the model and left open. Obviously, this requires that water is present in the solution, but it has been shown in [8] that the assumption that it is an MG that precipitates seems to be good even when at high methanol to water ratios.

The number for p is a parameter in this model. Its choice is not important regarding the description of the SLE, but it influences the kinetics. For all equilibrium calculations of the present work, the choice of [8] with $p = 9$ was adopted and the solid-liquid equilibrium is described by Equation 5.

$$K_9^{SL}(T) = \frac{x_W^L \cdot \gamma_W^L}{x_{MG,9}^L \cdot \gamma_{MG,9}^L} \quad (1)$$

Therein K_9^{SL} is the solubility constant, x_W^L and $x_{MG,9}^L$ are the true mole fraction of water and MG_9 in the liquid phase, and γ_W^L and $\gamma_{MG,9}^L$ are the activity coefficient of these components.

For the description of the kinetics, it is assumed that the equilibrium between the solid and liquid regarding MG_p is established at all times; i.e., no mass transfer, nucleation, or metastability limitations are considered. Kinetic effects are caused only by the reaction kinetics in the liquid phase. This is justified, as the overall kinetics are very slow. The reaction kinetic model was adopted from Ott [25], as described in [8]. The reaction kinetic model is activity-based and, hence, consistent with the SLE model, and accounts for the influence of both temperature and pH value.

The previous models were extended in the present work in two ways: firstly, OME was included in the model, which was straightforward, as OME is inert here, and the corresponding UNIFAC parameters were available from Schmitz et al. [26]. Secondly, the possibility of the formation of a second liquid phase was considered by taking into account the corresponding phase equilibrium

conditions. For the calculation of the liquid-liquid equilibrium, the iso-activity criterion is applied for the true components.

No model parameters were fitted to equilibrium data from the present work, hence corresponding model results are strict predictions. From [8] it is already known that the SLE in the system (formaldehyde + water) is well described by the model. The model results for the SLE in the system (formaldehyde + water + methanol) are predictions, as the solubility constant was only fitted to the data of the system (formaldehyde + water). In the concentration range that is relevant for the present work, the model describes the SLE in the system (formaldehyde + water + methanol) well [8]. The same holds for the kinetics of the solid formation in the systems (formaldehyde + water) and (formaldehyde + water + methanol). LLE in systems containing formaldehyde, water, methanol, and OME have been studied previously by Schmitz et al. [14]. The LLE model from the present work is identical with that of Schmitz et al. [14] and, therefore, describes the LLE generally well.

5. Results and discussion

5.1 Overview and numerical results

Experiments were carried out in the present work at 273.2, 283.0, 293.3 and 303.4 K in the ternary systems (formaldehyde + water + OME₂), (formaldehyde + water + OME₄) and the quaternary systems (formaldehyde + water + methanol + OME₂) and (formaldehyde + water +

methanol + OME₄). In some of the experiments with the ternary systems, the formation of a second liquid phase was observed.

The feed compositions in the ternary systems were chosen as follows. Starting with an aqueous formaldehyde solution with $\tilde{x}_{\text{FA}}^{(\text{m})} = 0.4 \text{ g g}^{-1} \text{ FA}$, three different amounts of OME were added. This resulted in three different overall fractions of OME in the solvent mixture ($\tilde{x}_{\text{OMEn,sol}}^{(\text{m})}$), consisting of water and OME. This quantity will be also used in the tables to characterize the feed compositions of each experiment. The experiments were then carried out for the different temperatures until equilibrium was reached.

In the quaternary systems, the feed compositions were chosen in a way that the water/methanol ratios were similar as in [8] and the OME fractions in the solvent mixture were varied in the same range as in the ternary systems.

The solid was always basically pure oligomeric formaldehyde. This was not proven by a direct analysis of the solid, which is very difficult due to its unstable nature, but it can be inferred from mass balance calculations using the feed composition and the composition of the liquid phase, which all indicated that the solid basically only contains formaldehyde, as shown below.

The numerical results of the experiments (starting compositions and time-dependent results for the liquid phase composition) are given in the Supporting Information.

In the following, we discuss first the results for the SLE and then those for the kinetics of the solid formation.

5.2 Solid-liquid equilibria

5.2.1 Ternary systems

Both SLE and SLLE were observed. High amounts of OME in the feed mixture and low temperatures favor the formation of the second liquid phase.

The results for the SLE and SLLE are given in Table 2 for OME₂ and in Table 3 for OME₄. The results are also visualized in Figure 2 together with data for the liquid-liquid equilibrium in the studied systems from Schmitz et al. [14].

Table 2: Feed compositions and liquid phase compositions in solid-liquid equilibria in the system (formaldehyde + water + OME₂); the solid is basically pure oligomeric formaldehyde. $\tilde{x}_{\text{FA}}^{(\text{m})}$ and $\tilde{x}_{\text{OME}_2}^{(\text{m})}$ are overall mass fraction of formaldehyde and OME₂, respectively. $\tilde{x}_{\text{OME}_2, \text{sol}}^{(\text{m})}$ is the overall OME₂ mass fraction in the solvent-mixture (here, water and OME₂). Equilibria with a second liquid phase are marked with an asterisk; the equilibrium composition belongs to the OME-rich liquid phase. Overall compositions are explained in Chapter 2. The feed compositions in simple mass fractions are given in the SI in Tables S-1 to S-10.

Experiment	T / K	feed composition		equilibrium composition	
		$\tilde{x}_{\text{FA}}^{(\text{m})} / \text{g g}^{-1}$	$\tilde{x}_{\text{OME}_2, \text{sol}}^{(\text{m})} / \text{g g}^{-1}$	$\tilde{x}_{\text{FA}}^{(\text{m})} / \text{g g}^{-1}$	$\tilde{x}_{\text{OME}_2}^{(\text{m})} / \text{g g}^{-1}$
1	273.2	0.3571	0.1562	0.1064	0.1373
2		0.3182	0.2935	0.0926	0.2618
3		0.2783	0.4150	0.0912*	0.2942*
4	283.0	0.3576	0.1569	0.1329	0.1291
Table 2 continued					
5		0.3179	0.2932	0.1186	0.2477

6	293.3	0.3573	0.1569	0.1655	0.1418
7		0.3178	0.2939	0.1458	0.2416
8		0.2782	0.4162	0.1373*	0.3052*
9	303.4	0.3465	0.1528	0.2039	0.1124

standard uncertainties u are $u(T)=0.1$ K, $u_r(\tilde{x}_{FA}^{(m)})=0.01$, $u(\tilde{x}_{OME2}^{(m)})=0.004$

Table 3: Feed compositions and liquid phase compositions in solid-liquid equilibria in the system (formaldehyde + water + OME₄); the solid is basically pure oligomeric formaldehyde. $\tilde{x}_{FA}^{(m)}$ and $\tilde{x}_{OME4}^{(m)}$ are overall mass fraction of formaldehyde and OME₄, respectively. $\tilde{x}_{OME4,sol}^{(m)}$ is the overall OME₄ mass fraction in the solvent-mixture (here, water and OME₄). Equilibria with a second liquid phase are marked with an asterisk; the equilibrium composition belongs to the OME-rich liquid phase. Overall compositions are explained in Chapter 2. The feed compositions in simple mass fractions are given in the SI in the Tables S-11 to S-22.

Experiment	T / K	feed composition		equilibrium composition	
		$\tilde{x}_{FA}^{(m)} / g\ g^{-1}$	$\tilde{x}_{OME4,sol}^{(m)} / g\ g^{-1}$	$\tilde{x}_{FA}^{(m)} / g\ g^{-1}$	$\tilde{x}_{OME4}^{(m)} / g\ g^{-1}$
10	273.2	0.3577	0.1561	0.1125	0.1363
11		0.3179	0.2937	0.1020*	0.2465*
12		0.2781	0.4164	0.1022*	0.2358*
13	283.0	0.3578	0.1566	0.1330	0.1367
14		0.3181	0.2930	0.1249*	0.2445*
15		0.2778	0.4162	0.1220*	0.2286*
16	293.3	0.3571	0.1584	0.1636	0.1334
17		0.3177	0.2929	0.1478*	0.2404*
18		0.2779	0.4167	0.1486*	0.2479*
19	303.4	0.3573	0.1574	0.1989	0.1222
20		0.3178	0.2939	0.1795	0.2350
21		0.2777	0.4167	0.1670*	0.2624*

standard uncertainties u are $u(T)=0.1$ K, $u_r(\tilde{x}_{FA}^{(m)})=0.01$, $u(\tilde{x}_{OME4}^{(m)})=0.004$

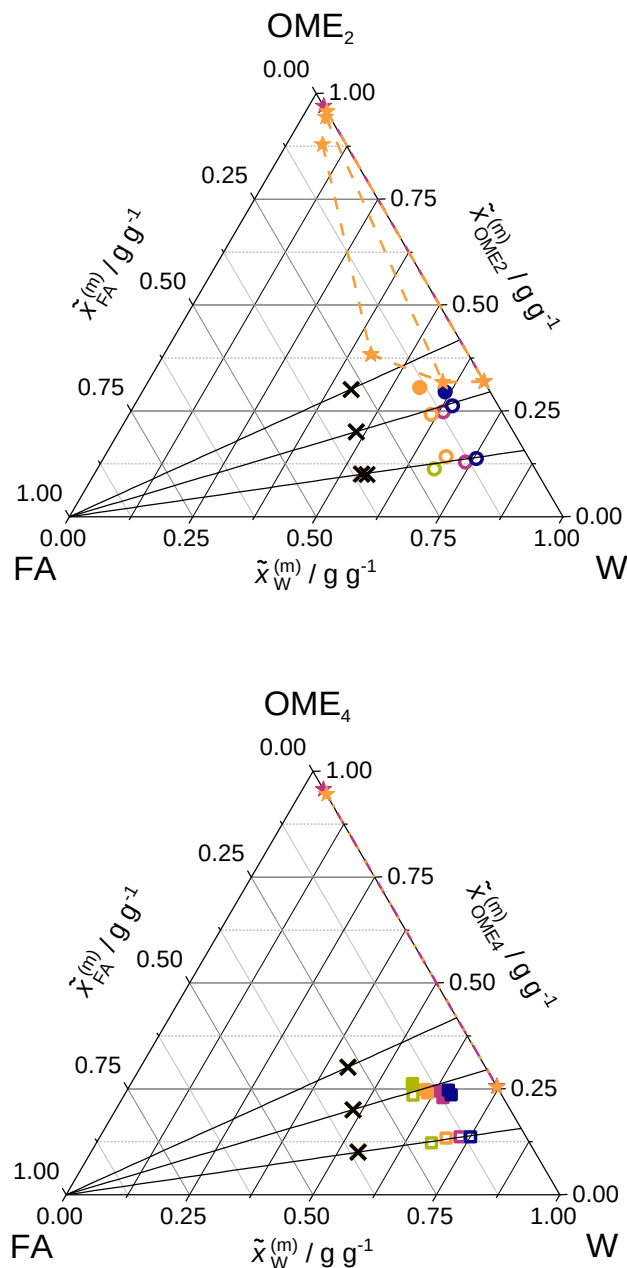


Figure 2: Results from experimental studies of the SLE and SLLE in the system (formaldehyde + water + OME₂, top) and (formaldehyde + water + OME₄, bottom). The numerical data of this work is given in Table 2 and 3. Crosses indicate feed compositions. Colored symbols: liquid phase compositions in SLE (empty) and SLLE (full, only data for the water-rich phase were measured). The solid lines are lines with a constant water/methanol ratio, namely that of the feed composition.

The fact that also the compositions of the homogeneous liquid phases lie on these lines indicates that the solid contains in all cases basically only CH_2O . For the feed with the highest OME content, the liquid split in two phases, of which only one was analyzed. Dotted lines with stars are results from Schmitz et al.[14] for tie lines of the LLE in the studied systems (for OME₄ only data for the formaldehyde-free binary system is available). The color refers to the temperature: (green) 393.4 K, (orange) 293.3 K, (magenta) 283.0 K, (blue) 273.2 K.

At low OME concentrations in the feed, SLE were observed, but upon increasing the OME concentration also SLLE occurred. In the formaldehyde-free binary systems as well as in the both ternary systems, the formation of a second liquid phase occurs earlier for OME₄ than for OME₂. As expected, the solubility of formaldehyde increases with increasing temperature. The influence of OME on the formaldehyde solubility is difficult to discern from Figure 2 and is discussed below in more detail.

For all SLE experiments, the mass balance lines through the liquid phase and the feed meet (within the limits of the uncertainty of the data) in a single point, which is pure formaldehyde, indicating that the solid is oligomeric formaldehyde. For simplicity, in Figure 2, not the individual mass balance lines are shown, but a line of a constant water/OME ratio through the feed, which also goes through the homogenous liquid phases. This is in agreement with the findings from [8]. In the SLLE, the data obtained for the system (formaldehyde + water + OME₂) for the liquid phase agree fairly well with the literature data for the LLE in that system from Schmitz et al. [14]. For OME₄ Schmitz et al. [14] only report data for the formaldehyde-free subsystem. As explained in the experimental section, only the water-rich liquid phase in the SLLE could be analyzed in the present work.

For a better assessment of the formaldehyde solubility in the studied solutions, Figure 3 shows the liquidus temperature of the solutions as a function of the overall formaldehyde mass fraction. The SLE data from the present work for mixtures containing OME₂ and OME₄ are presented together with data for the system (formaldehyde + water) from [8]. The results clearly show that adding OME leads to a reduction of formaldehyde solubility. The differences between adding OME₂ and OME₄ are not large, and no systematic trend can be discerned from the available data. As expected, increasing the temperature has a strong effect on the formaldehyde solubility.

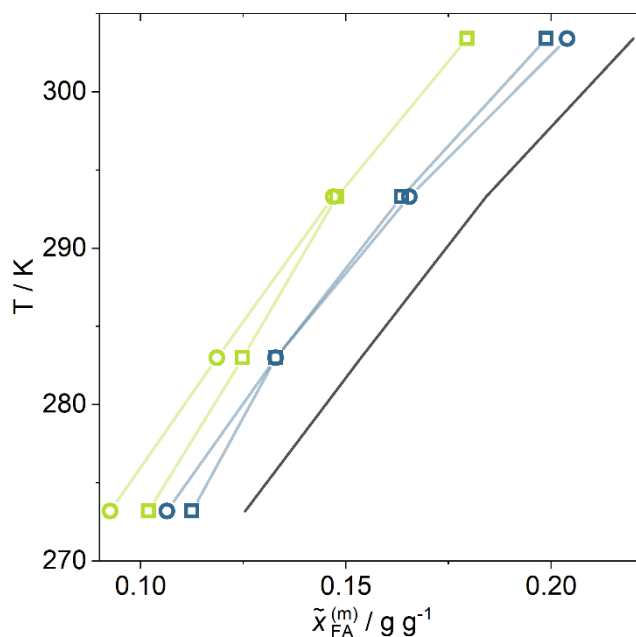


Figure 3: Experimental liquidus temperature as a function of the overall mass fraction of formaldehyde for the systems (formaldehyde + water + OME₂) (circles) and (formaldehyde + water + OME₄) (squares). The numerical data of this work is given in Table 2 and 3. The color indicates the OME mass fraction in the solvent mixture: (blue) 0.156 g g⁻¹, (green) 0.293 g g⁻¹. The solid black line indicates data for the system (formaldehyde + water) from [8]. All lines are linear splines.

It is important to note, that the results shown in Figure 2 and 3, as well as all other SLE and SLLE results from the present work, refer to long-term behavior of the solutions. If only the short-term solubility is considered, with time constants of minutes or hours, much higher values of the formaldehyde concentrations in homogenous liquid solutions can be obtained, see Breitzkreuz et al. [8] for a discussion.

The comparison of the results for the studied ternary systems with those for the binary system (formaldehyde + water) shows that the curves are basically only shifted. This indicates that the reduction of the solubility could simply be caused by the replacement of the good solvent water with the poor solvent OME. This can be seen better in Figure 4 which gives a magnified view of the data from Figure 2 and additionally includes two sorts of lines. The solid lines were obtained from the model and are discussed below. The dashed lines indicate simply a constant formaldehyde/water mass ratio. Each of the lines starts at the solubility of formaldehyde in pure water at the studied temperature, which was from [8], (stars), and ends in pure OME. As basically all experimental data points fall approximately on these lines, it can be concluded that the solubility of formaldehyde in solutions containing OME can be found from the solubility of formaldehyde in pure water, simply by a mapping using the formaldehyde/water mass ratio, cf. Figure 4.

Also, the results from the physico-chemical model are shown in Figure 4. Considering the fact that the model results are pure predictions and no data from the present work was used for its training the agreement is very good. Even though slightly less accurate than the empirical construction described above, the basic facts regarding the formaldehyde solubility in the studied systems are predicted well.

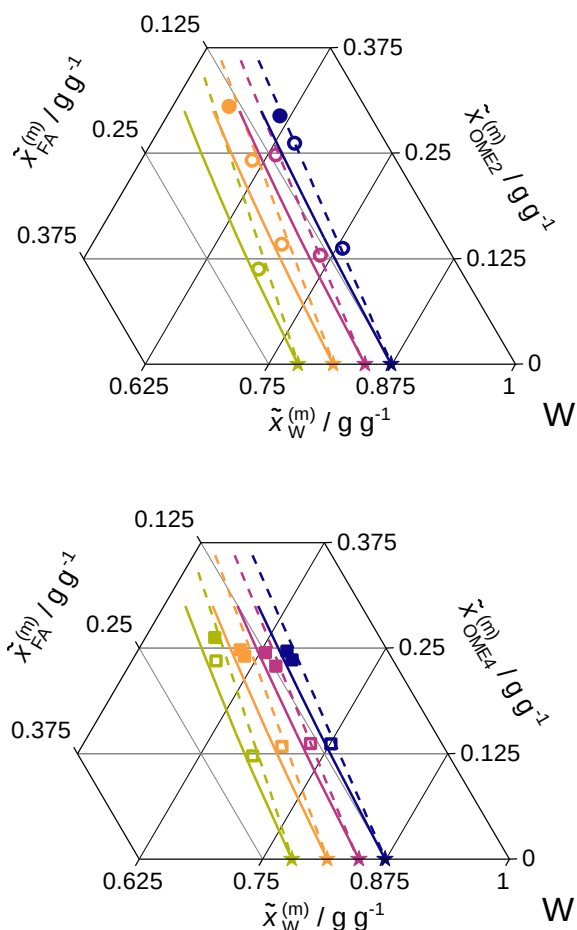


Figure 4: Magnified view of the experimental data shown in Figure 2. Additionally, two types of lines are shown. Solid lines show the solubility calculated by the model. Dashed lines are linear connections of the experimental solubility in the system (formaldehyde + water) with pure OME, i.e., they are lines of constant mass ratio of formaldehyde/water. Top: (formaldehyde + water + OME₂), Bottom: (formaldehyde + water + OME₄). Open symbols: SLE, filled symbols: SLLE. The color refers to the temperature: (green) 393.4 K, (orange) 293.3 K, (magenta) 283.0 K, (blue) 273.2 K.

All in all, the observations indicate a phase behavior of the studied systems as shown schematically in Figure 5. In that phase diagram, the SLE region for low water concentrations is speculative, as no corresponding data are available.

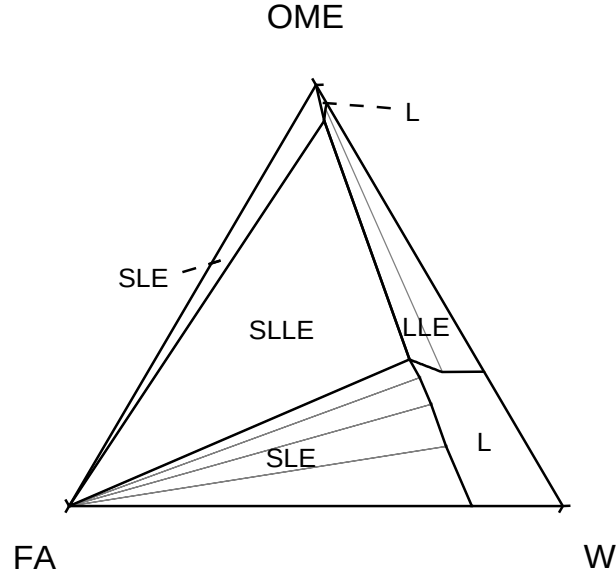


Figure 5: Qualitative phase diagram for mixtures of (formaldehyde + water + OME) for the conditions under which the measurements were carried out. Thin lines are tie lines and thick lines distinguish the different equilibrium areas. The feed of the equilibrium experiments of the present work was either in the SLE region at the (formaldehyde + water)-side of the diagram (homogenous liquid phase, SLE), or in the three phase region (two liquid phases, SLLE).

5.2.2 Quaternary systems

An overview of the samples and the corresponding equilibrium compositions of the liquid phase for the system (formaldehyde + water + methanol + OME) is given in Table 4.

Table 4: Feed compositions and liquid phase compositions in solid-liquid equilibria in the system (formaldehyde + water + methanol + OME). $\tilde{x}_{\text{FA}}^{(m)}$, $\tilde{x}_{\text{MeOH}}^{(m)}$, and $\tilde{x}_{\text{OME}_n}^{(m)}$ are overall mass fraction of formaldehyde, methanol, and OME₄, respectively. $\tilde{x}_{\text{OME}_n, \text{sol}}^{(m)}$ is the overall OME_n mass fraction in

the solvent-mixture (here, water, methanol, and OME_n). Overall compositions are explained in Chapter 2. The feed compositions in simple mass fractions are given in the SI in Tables S-23 to S-33.

Experi- ment	OME _n	T / K	feed composition			equilibrium composition		
			$\tilde{x}_{\text{FA}}^{(\text{m})} /$ g g ⁻¹	$\frac{\tilde{x}_{\text{MeOH}}^{(\text{m})}}{\tilde{x}_{\text{W}}^{(\text{m})}}$	$\tilde{x}_{\text{OMEn,sol}}^{(\text{m})} /$ g g ⁻¹	$\tilde{x}_{\text{FA}}^{(\text{m})} /$ g g ⁻¹	$\tilde{x}_{\text{W}}^{(\text{m})} /$ g g ⁻¹	$\tilde{x}_{\text{OMEn}}^{(\text{m})} /$ g g ⁻¹
22	4	273.2	0.3783	0.1579	0.1685	0.1698	0.5956	0.1379
23			0.3376	0.1580	0.3020	0.1516	0.5119	0.2541
24			0.4118	0.3901	0.1701	0.2370	0.4506	0.1811
25			0.3656	0.3924	0.3164	0.2069	0.3975	0.2461
26		293.3	0.3803	0.1576	0.1613	0.2328	0.5572	0.1207
27			0.3377	0.1588	0.3021	0.2057	0.4786	0.2379
28			0.4117	0.3898	0.1705	0.2989	0.4219	0.1175
29			0.3655	0.3896	0.3159	0.2534	0.3706	0.2335
30	2	273.2	0.3801	0.1573	0.1615	0.1710	0.5977	0.1319
31			0.3374	0.1576	0.3024	0.1521	0.5123	0.0833
32			0.4118	0.3904	0.1705	0.2349	0.4558	0.1809

standard uncertainties u are $u(T)=0.1$ K, $u_r(\tilde{x}_{\text{FA}}^{(\text{m})})=0.01$, $u_r(\tilde{x}_{\text{W}}^{(\text{m})})=0.02$, $u_r(\tilde{x}_{\text{MeOH}}^{(\text{m})})=0.02$, $u(\tilde{x}_{\text{OMEn}}^{(\text{m})})=0.004$

In principle, concentrations in a quaternary system can be represented in a tetrahedron. We prefer to use projections of the points on sides of the tetrahedron for the representation. As shown schematically in Figure 6. Two projections are used, one onto the formaldehyde-free system (W + MeOH + OME) (blue in Figure 6) and a second onto the OME-free system (FA + W + MeOH) (red in Figure 6).

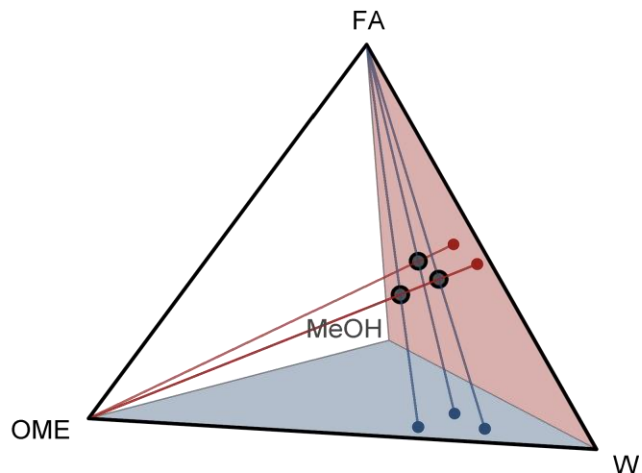


Figure 6: Sketch of the projections used to represent the results for concentrations in the quaternary system (formaldehyde + water + methanol + OME).

Figure 7 shows the results of the projection of feed compositions and equilibrium compositions obtained in the experiments with quaternary mixtures onto the formaldehyde-free ternary system. Results for OME₂ and OME₄ for 273 and 293 K are shown. As can be seen, the projections of the equilibrium compositions and the feed compositions agree perfectly well. This strongly supports the hypothesis that the formed solid is pure oligomeric formaldehyde.

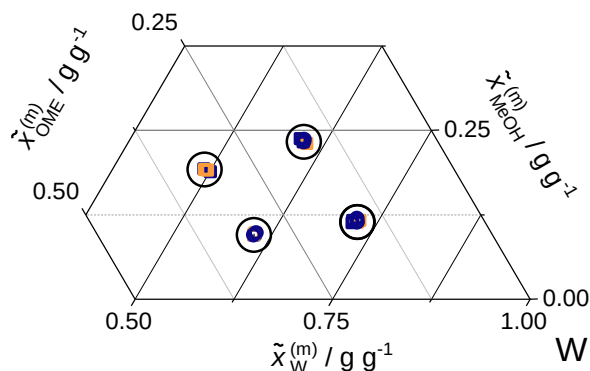


Figure 7: Projection of the feed composition (black cycles) and the liquid phase composition in solid-liquid equilibrium in the quaternary system (formaldehyde + water + methanol + OME) onto the formaldehyde-free ternary system (blue triangle in Figure 6). Results for OME₂ (circles) and OME₄ (squares) for 273.2 (blue) and 293.3 K (orange) are shown. The numerical data is given in Table 4. The radius of the symbol for the projection of the feed composition is 0.025 g g⁻¹ which corresponds to around twice the experimental uncertainty of the measurement. The agreement between the projections of the equilibrium and the feed compositions supports the hypothesis that the precipitating solid is pure oligomeric formaldehyde.

Figure 8 shows the results of the projection of the equilibrium compositions obtained in the experiments with quaternary mixtures onto the OME-free ternary system. In addition to the results from the present work, also results obtained in [8] for the system (formaldehyde + water + methanol) are shown (crosses and solid lines). In the projection, they coincide with the results for the quaternary system, indicating that, also here, the formaldehyde solubility can be inferred from the solubility in the OME-free systems, as for the studied ternary systems.

Additionally, the solubilities calculated with the model are shown. The dotted line shows the calculated solubility for the ternary system (formaldehyde + water + methanol) and the dashed line

the calculated solubility for the system (formaldehyde + water + methanol + OME₄) with an OME₄ fraction in the solvent mixture of 0.3 g g⁻¹. The results for OME₂ are almost identical to those for OME₄ and are therefore not included in Figure 8, where both sets could not be discerned. All in all, the model predicts the experimental results well. Again, it should be considered that no data from the present work was used for training the model. The results for the SLE in the quaternary system were obtained using a model that was only trained with SLE data from the system (formaldehyde + water).

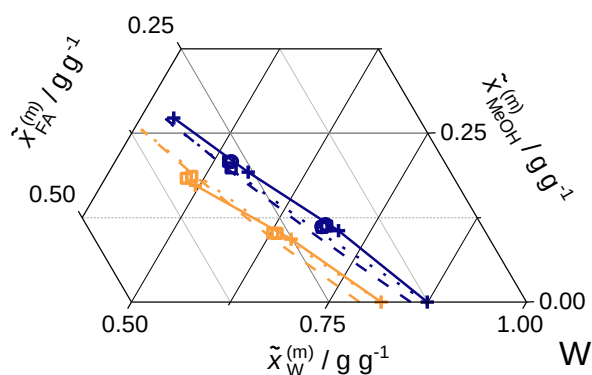


Figure 8: Projection of the liquid phase composition in solid-liquid equilibrium in the quaternary system (formaldehyde + water + methanol + OME) onto the OME-free ternary system (red triangle in Figure 6). Results for OME₂ (circles) and OME₄ (squares) are shown. The numerical data is given in Table 4. Crosses with straight lines show results for the system (formaldehyde + water + methanol) from [8]. The color corresponds to the temperature: (blue) 273.2, (orange) 293.3 K. Dotted lines show the results from the physico-chemical model for the system (formaldehyde + water + methanol), and the dashed lines those for the system (formaldehyde + water + methanol + OME₄) with an OME₄ fraction in the solvent mixture of 0.3 g g⁻¹.

5.3 Kinetics of solid formation

In addition to determining the equilibrium, the measured overall concentration profiles over time can also be used to evaluate the kinetics of solid formation. However, the investigation of the kinetics of the solid precipitation was not the primary target of the present study. The pH value was chosen high, in order to accelerate the kinetics. Therefore, in many of the experiments, the equilibrium value was already almost reached in the first sample that was analysed, so that only little information on the kinetics was obtained.

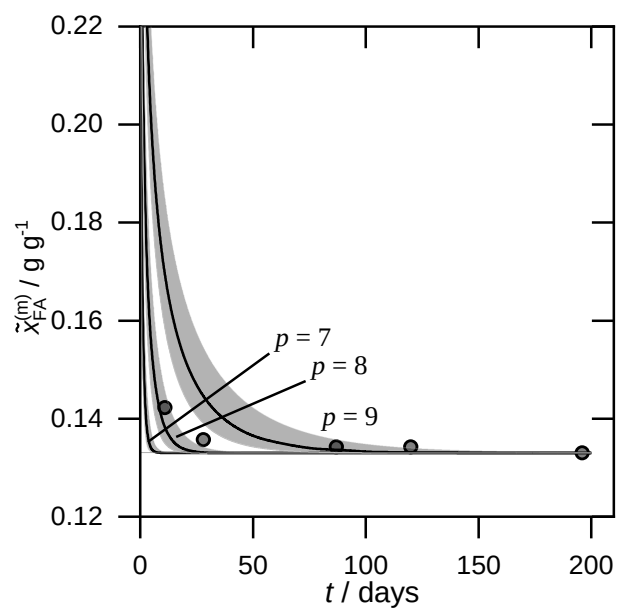
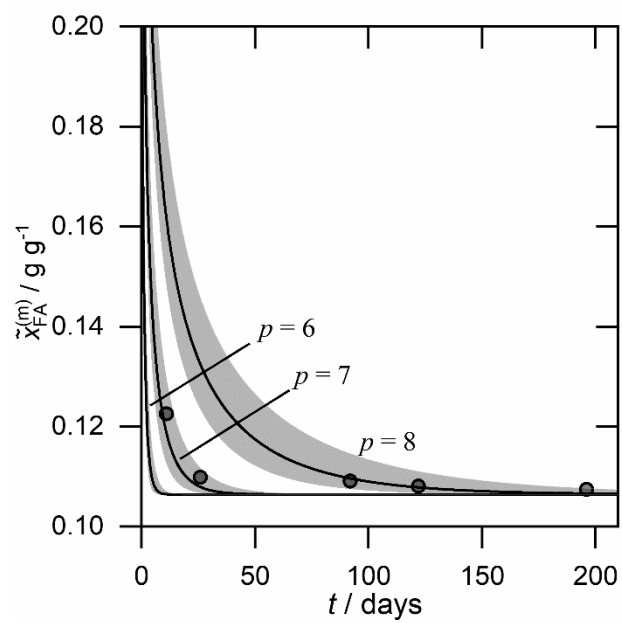
In the previous work [8], it was already shown that it is possible to describe the measured concentration profiles over time for OME-free systems with the physico-chemical model presented above. The kinetic model is primarily based on the reactions kinetics of the oligomer formation. For their description, the reaction kinetic model of Ott [25] was used, which account both for the temperature dependence and the dependence on the pH value. The model was fitted to experiments with a pH of up to 7. Nevertheless, in the previous work [8], the model was used for pH values up to about 9.5. To further accelerate the kinetics, the pH value was about 11 in the present work, which is clearly far out of the range for which the kinetic model of Ott [18,25] was parameterized. Nevertheless, it was applied – but the results should be interpreted cautiously. The only further model parameter that influences the kinetics is the choice of the chain length p of the precipitating methylene glycol MG_p .

Figure 9 shows a comparisons between the measured and calculated concentration profiles for the Experiments 1,13, and 27. The results for the experiments that are not shown in Figure 9 are presented in the Supporting Information. Model results are presented for different choices of p ;

furthermore, also the pH value was varied, results are shown for the pH value 11 ± 1.5 . The simulations were carried out in the same way as described in [8].

For the experiments shown in the top and middle panel of Figure 9 the variation of the concentration of the solution over time can be discerned, for the experiment in the bottom panel, the concentration remains basically constant, i.e., equilibrium was already reached at the time the first analysis was carried out, which was after about 60 days. The question can be raised, why the analysis was not carried out at shorter intervals. The reason is that with each analysis the mass of the sample reduces and a certain amount is needed for the handling.

In the two experiments shown in the upper two panels in Figure 9, the best agreement between the model predictions and the data is observed for $p = 7$ (top) and $p = 8$ (middle), respectively, which is not far from the value $p = 9$ recommended in [8]. From the experiment shown in the bottom panel of Figure 9, which was so fast that no change in concentration was monitored, only a statement on an upper limit for the choice of p can be made: it can be inferred from the results that p cannot be higher than 10, which is in line with the other findings.



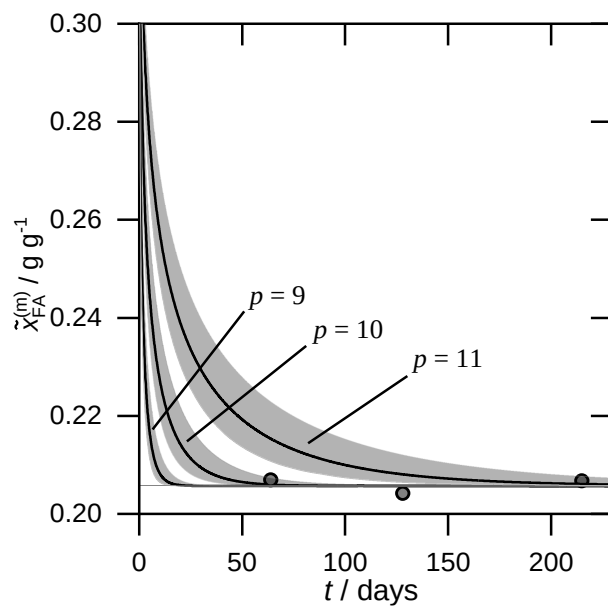


Figure 9: Overall formaldehyde concentration in the liquid phase for different experiments. Top: Experiment 1, middle: Experiment 13, bottom: Experiment 27. Points are experimental data. Solid lines are calculated for different values of the chain length p of the precipitating MG_p . The grey area shows the influence of variations of the pH by ± 1.5 .

Figure 10 shows the best fitting value for p for all experiments, beside the experiments with the two liquid phases. The resulting values for p that were found show a dependency on the temperature.

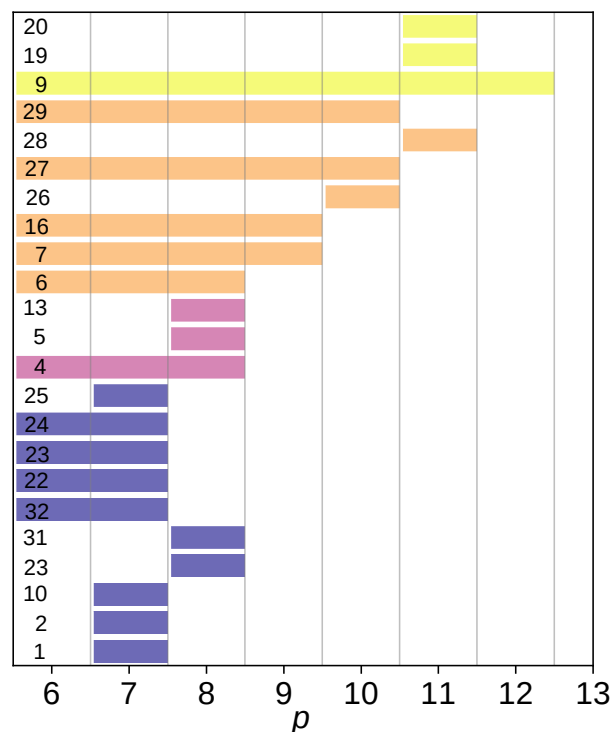


Figure 10: Optimal values for p obtained from the kinetic fits. The line number indicates the number of the experiment. Bars indicate that only an upper limit of p could be determined. The color represents the temperature of the experiment: (■) 303.4 K, (■) 293.3 K, (■) 283.0 K, (■) 273.2 K.

It can be seen from Figure 10 that the values found for p depend on the temperature; the highest values for p are found for the highest temperature, the lowest for the lowest temperature. For a given temperature, the optimal value of p generally varies only between two neighboring values. The temperature trend is probably caused by deficiencies of the reaction kinetic model, which was used outside the range for which it was trained. Keeping this in mind, the results shown in Figures 9 and 10 are quite satisfactory and indicating that the model reflects essential features of the formation of the solid and should be applicable in regions for which the reaction kinetic model has been validated.

6. Conclusions

The formation of solids is a ubiquitous problem in formaldehyde technology. Despite its technical importance, neither the conditions under which solids form in formaldehyde solutions, nor the mechanisms were known until recently. This has changed with a work [8] of our group on the systems (formaldehyde + water) and (formaldehyde + water + methanol), in which the problem was tackled both from the experimental side and by physico-chemical modeling and simulation. Both the solid-liquid equilibrium and the kinetics of the solid formation in the studied systems can be described now. In the present work, we have extended the approach established in [8] to systems containing formaldehyde, water, methanol, and OME. OME are promising new synthetic fuels that can be made from aqueous formaldehyde solutions and methanol by efficient processes [6,26]. In these processes, it is important to avoid any formation of unwanted formaldehyde solids. The present work lays the foundations for this.

Solid liquid equilibria and kinetics of the solid formation were studied in mixtures containing (formaldehyde + water + OME) and (formaldehyde + water + methanol + OME) at temperatures between 273 to 303 K. The experiments were carried out with OME₂ and OME₄. The solid is difficult to analyze, but the analysis of the results based on mass balances clearly indicates that the solid is basically pure oligomeric formaldehyde. In the ternary mixtures, beside SLE, an SLLE was observed. The findings on the LLE are in line with those from previous work by Schmitz et al. [14].

Adding OME reduces the solubility of formaldehyde, and the reduction does not significantly depend on whether OME₂ or OME₄ is used. The interpretation of this empirical finding is that

OME is a poor solvent for formaldehyde and basically only dilutes the good solvents water and methanol. It can be assumed that this finding holds not only for OME₂ and OME₄, but for all OME.

The physico-chemical model from [8] was extended in the present work to include OME, without adjusting any model parameters to the present SLE and SLLE data, which are predicted astonishingly well. This suggests that the model assumptions are reasonably chosen.

In the experiments, also information on the kinetics of the solid formation was obtained. The kinetics of the solid formation are slow. As they are mainly determined by the liquid phase reaction kinetics, they can be accelerated by acids or bases acting as catalysts. Despite the use of such catalysts, the experiments took up to 500 days. The kinetic model describes the results well, but only after an adjustment of a model parameter (the number of CH₂O segments in the precipitating species, which is always an oligomer of formaldehyde and water). The findings from [8] that p is about 9 was basically confirmed.

In future work, it would be desirable to obtain information on the solid formation in the studied systems in a wider temperature range and more kinetic data. The results from the present work enable a rational assessment of risks regarding the formation of solids in OME production processes. They provide a basis for an adapted design of the process and the equipment, and a suitable choice of operating windows.

Nomenclature

Abbreviations

FA	Formaldehyde
HF	Poly(oxymethylene)hemiformals
LLE	Liquid-liquid equilibrium
MeOH	Methanol
MG	Poly(oxymethylene)glycols
OME	Poly(oxymethylene)dimethyl ether
SLE	Solid-liquid equilibrium
SLLE	Solid-liquid-liquid equilibrium
UNIFAC	Universal Quasichemical Functional Group Activity Coefficients
W	Water

Symbols and indices

a_i^L	Activity of component i in the liquid phase
γ_i^L	Activity coefficient of component i in the liquid phase
K_p^{SL}	Solubility constant for poly(oxymethylene)glycol of chain length p
x_i^L	Mole fraction of component i in the liquid phase
$\tilde{x}_i^{(m)}$	Overall mass fraction of component i
$\tilde{x}_{i,sol}^{(m)}$	Overall mass fraction of component i in the solvent mixture

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Supporting Information

Numerical data of the measurements

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