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Equilibrium Speciation in Moderately Concentrated Formaldehyde–Methanol–Water Solutions Investigated Using ^{13}C and ^{1}H Nuclear Magnetic Resonance Spectroscopy

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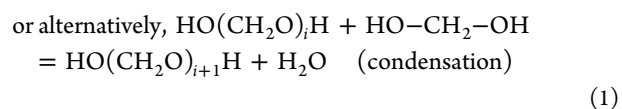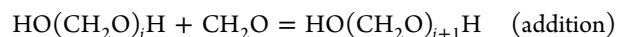
S *Supporting Information*

ABSTRACT: We used ^{13}C and ^{1}H NMR spectroscopy to examine the equilibrium speciation in formaldehyde–methanol–water solutions at moderate formaldehyde concentrations such as those used in the synthesis of formaldehyde-based organic gels. Concentrations of small methylene glycol oligomers and their methoxylated forms found in these solutions were quantitatively determined over a range of formaldehyde concentrations and methanol–water ratios, and at temperatures between 10 and 55 °C. Using the measured concentrations, equilibrium constants for methylene glycol dimer and trimer formation as well as methoxylation of these oligomers were calculated. Based on this, we developed a quantitative equilibrium model for calculation of formaldehyde-related species concentrations over a range compositions relevant for formaldehyde based sol–gel processes allowing for more rational design of formaldehyde polymerization systems.

■ INTRODUCTION

Formaldehyde is widely used as a reactant in the synthesis of a range of polymeric materials, including formaldehyde-based resins as well as novel nanoporous organic gels.[1,2] Synthesis of these materials is typically based on commercially available aqueous-methanolic formaldehyde solutions and other reactants, such as phenol, melamine, urea, and cresol.[3] Since one can vary the nature and concentration of reactants as well as any additives (such as catalysts) and also reaction time and temperature, the variety of resulting materials is virtually limitless. Designing a synthesis process is often a goal-oriented task, in which one aims to obtain a material possessing specific properties by adjusting available process parameters. This is often done through design of experiments design using various degrees of systematic approach. On the other hand, in order to better understand, design, and optimize sol–gel processes involving formaldehyde solutions, molecular speciation in formaldehyde solutions needs to be quantitatively understood.

Industrial production of formaldehyde is most commonly carried out by means of the catalytic oxidation of methanol in air. The resulting gaseous mixture of formaldehyde and methanol is absorbed into water, forming an aqueous–methanolic solution of formaldehyde, which is stable over a wide range of compositions. In laboratory studies, solid paraformaldehyde (polymerized formaldehyde) is often used for preparation of formaldehyde solutions. In aqueous solutions, formaldehyde undergoes hydration, forming methylene glycol, which is subject to further condensation to form oligomers,[4,5] as shown in eq 1.

$$HO-CH_2-OH \quad \text{(hydration)}$$

$$HO(CH_2O)_iH + CH_2O = HO(CH_2O)_{i+1}H \quad \text{(addition)}$$

$$\text{or alternatively, } HO(CH_2O)_iH + HO-CH_2-OH$$
$$= HO(CH_2O)_{i+1}H + H_2O \quad \text{(condensation)}$$

$$(1)$$

Formation of glycols and oligooxyglycols in formaldehyde solutions in water.

The formaldehyde hydration equilibrium constant is relatively large (around 2000 at ambient temperature[5]), and so, formaldehyde in its aldehyde form is present only in trace amounts, typically smaller than 100 ppm.[3] Stable aqueous solutions of formaldehyde therefore contain methylene glycol and its oligomeric forms, which are in mutual equilibria. Under such conditions, oligomerization reactions can be described interchangeably as either formaldehyde addition or methylene glycol condensation. However, in order to determine relevant equilibrium constants, concentrations of all species involved need to be measured quantitatively. Therefore, in accordance with previous studies reported in literature, we will further use the methylene glycol condensation formalism. The extent of oligomerization of methylene glycols can be controlled by the presence of an alcohol (ROH), which reacts reversibly with

methylene glycols to form singly and doubly alkoxylated glycols (hemiacetals and acetals, respectively), where hydroxyl groups are replaced by alkoxy groups (RO−), as shown in eq 2.

$$HO(CH_2O)_iH + R-OH = RO(CH_2O)_iH + H_2O$$

$$RO(CH_2O)_iH + R-OH = RO(CH_2O)_iR + H_2O \qquad (2)$$
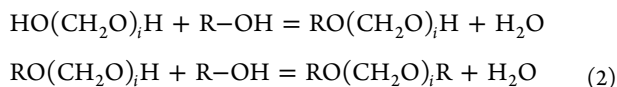
Formation of hemiacetals and acetals through alkoxylation of methylene glycol oligomers.

We note that formation of doubly alkoxylated methylene glycols (acetals) is kinetically unfavorable, and thus, these have not been observed experimentally in methanol−water formaldehyde solutions, except under acid catalyzed conditions below pH around 3.[6−9] Trioxane, an anhydrous cyclic trimer of formaldehyde, can also form at elevated temperatures in water−methanol solutions under acid catalysis.[10,11]

Formation of singly alkoxylated methylene glycols shifts the overall speciation equilibrium toward smaller species and limits formation of larger oligomers. Commercially available formaldehyde solutions are typically stabilized with a sufficient amount of methanol. Therefore, knowledge of equilibrium constants of condensation and alkoxylation reactions is required in order to quantitatively predict speciation in formaldehyde solutions and in methanol−water solutions.

To date, the speciation of formaldehyde−methanolic aqueous solutions used for the synthesis of organic gels has not been widely studied, despite a vast number of reported applications. Previously published work dealt with quantitative determination of speciation in formaldehyde solutions and was focused on solutions at much higher formaldehyde concentrations (typically between 30% and 70% by weight). These were usually prepared by absorbing gaseous formaldehyde or by depolymerization of poly(oxymethylene) in water[12−14] or less frequently in methanol.[3,15,16] Only a few former studies considered using either less concentrated formaldehyde aqueous solutions (down to 2% by weight[17]) or mixed aqueous−methanolic solutions.[15,18,19] However, formaldehyde solutions used in the synthesis of organic gels are typically prepared by dilution of commercially available aqueous solutions of formaldehyde (30−40% by weight) stabilized by methanol (10−15% by weight). We have recently investigated oligomerization and mesoscale clustering in dilute formaldehyde solutions in the presence of sodium carbonate, which is typically used as basifying agent in resorcinol−formaldehyde polymerization, at a fixed formaldehyde concentration and temperature. We have found that in the presence of sodium carbonate, mesoscale clusters of colloidal dimensions are formed, although dimerization and methoxylation equilibria do not appear to be affected.[20,21] The motivation for extending our research (this report) was to investigate speciation in moderately concentrated formaldehyde solutions over a range of concentrations and temperatures. This would enable the development and validation of a quantitative equilibrium speciation model and thus allow accurate modeling of sol−gel processes involving formaldehyde solutions. Quantitative determination of formaldehyde related species in such solutions have not been previously reported and neither was an equilibrium speciation model available in literature and experimentally validated under such conditions.

A number of spectroscopic methods have been used to investigate formaldehyde solutions, including IR, Raman, and UV−vis spectroscopies as well as Nuclear Magnetic Resonance (NMR). While IR and Raman can be used to determine total formaldehyde and alcohol concentrations, they have so far provided largely qualitative information on formaldehyde.[12,22] UV−vis is suitable for determination of free formaldehyde, since the carbonyl group of the free formaldehyde molecule can be conveniently monitored at 290 nm.[23] This was widely used in previous studies.[24−30]

NMR has been very useful for quantitative determination of formaldehyde oligomeric species in solutions due to its superb sensitivity at the nucleus level. We found only one paper in the previous literature[18] dealing with ^{1}H NMR spectroscopy of formaldehyde−water−methanol solutions (formaldehyde concentrations 37% by weight and higher), providing signal assignments for methylene glycol oligomers up to trimers as well as their methoxylated forms. Aqueous solutions of formaldehyde have been more widely studied by ^{1}H NMR spectroscopy. In one of the early papers,[17] a wide range of formaldehyde concentrations (between 2% and 60% by weight in D_2O solutions) was considered and quantitative speciation information was obtained at lower formaldehyde concentrations. The authors also reported corresponding oligomerization equilibrium constants. In a later study,[31] both ^{1}H and ^{13}C NMR were used and signal assignment of methylene glycol oligomers in aqueous formaldehyde solutions (35% by weight and higher) were provided for both nuclei. Additionally, relaxation times (T_1) were also reported. It was also noted that for highly concentrated formaldehyde solutions, ^{13}C NMR may be superior to ^{1}H NMR in terms its ability to quantitatively distinguish between larger oligomers due to its superior sensitivity to local molecular environments. Following on from a series of papers on studies of formaldehyde solutions published in the former Soviet Union, Balashov and co-workers[19] investigated speciation of formaldehyde in mixtures of water and alcohols (including methanol, ethanol, and ethylene glycol) using ^{13}C NMR. They reported equilibrium constants for oligomerization of methoxylated methylene glycol species in highly methanolic solutions at relatively high formaldehyde concentrations.

A notable series of publications on methylene glycol equilibria was published by Maurer and co-workers starting in the 1990s. These focused on ^{13}C and ^{1}H NMR as quantitative tools to describe the speciation of aqueous solutions of formaldehyde and underpinned the development of equilibrium speciation models. Earlier studies,[4,15] focused on equilibria of formaldehyde related species in solutions of water, deuterium oxide, and methanol, respectively. In further work, NMR data on speciation in formaldehyde−water and formaldehyde−methanol solutions were used to develop thermodynamic models of vapor−liquid equilibria in formaldehyde−water−methanol systems.[32] However, when these models were compared with later ^{13}C NMR measurements on formaldehyde−water−methanol solutions (at formaldehyde concentration of 27.5% by weight and higher), it resulted in less than satisfactory agreement of predicted and measured species concentrations.[33] We note that this work also reported detailed assignments of ^{13}C NMR signals for formaldehyde related species in mixed water−methanol solutions, referring to two-dimensional heteronuclear [1]H−[13]C correlation experiments (results of which were not shown). In a following article,[34] ^{1}H NMR spectroscopy was proposed for fast and accurate online reaction and process monitoring. This was further explored by Ott et al.[16] who used ^{1}H NMR to investigate the kinetics of oligomerization reactions in solutions of formaldehyde over a range of temperatures and a range of pH values. In another

Table 1. Composition of Formaldehyde Solutions Investigated by NMR

sample	H$_2$O added [mL]	methanol added [mL]	D$_2$O added [mL]	formaldehyde stock solution [mL]	formaldehyde mole fraction	methanol mole fraction	water (H$_2$O + D$_2$O) mole fraction
F−W 1−3	2.10	0	0.90	1.00	0.063	0.021	0.917
F−W 1−6	4.20	0	1.80	1.00	0.035	0.012	0.953
F−W 1−10	7.00	0	3.00	1.00	0.022	0.007	0.970
F−W 1−30	21.0	0	9.00	1.00	0.008	0.003	0.990
F−W 1−60	42.0	0	18.0	1.00	0.004	0.001	0.995
F−M 1−3	0	3.00	1.00	1.00	0.076	0.442	0.483
F−M 1−6	0	6.00	1.50	1.00	0.048	0.546	0.406
F−M 1−10	0	10.0	2.00	1.00	0.033	0.619	0.348
F−M 1−30	0	15.0	3.00	0.50	0.012	0.664	0.324
F−M 1−60	0	30.0	6.00	0.50	0.006	0.677	0.317

study,[10] ^{1}H NMR spectroscopy was used to quantitatively investigate the reaction kinetics of formation and decomposition of 1,3,5-trioxane in methanol-free aqueous formaldehyde solutions. Despite a number of papers on the formaldehyde aqueous solutions, work previously published by others has focused on highly concentrated solutions of formaldehyde, while little attention has been paid to moderately concentrated formaldehyde−methanol−water solutions, such as those used in sol−gel polymerization of formaldehyde and resorcinol or phenol.[1,2,35,36]

In this work, we present detailed investigations of speciation in formaldehyde−water−methanol solutions over a range of concentrations and temperatures using ^{1}H and ^{13}C NMR spectroscopy. While both ^{1}H and ^{13}C NMR in principle allow for resolution of small oligomers present in the solutions investigated, we discuss the utility of ^{1}H NMR for rapid quantitative monitoring of formaldehyde related species in mixed aqueous methanolic solutions at variable temperatures. This is with a view to enabling *in situ* monitoring of the kinetic processes involved in the synthesis of formaldehyde-based organic gels. Solutions with total formaldehyde concentrations of 0.39−3.08 mol/dm^3 (mole fractions 0.005−0.076) were investigated over a range of water−methanol solvent compositions and temperatures (10−55 °C) and quantitative species distributions were determined. This allowed equilibrium constants for dimer and trimer formation to be estimated as well as for their methoxylated forms found in water−methanol solutions. The resulting equilibrium speciation model allows quantitative prediction of speciation in formaldehyde solutions typically encountered in sol−gel polymerization of formaldehyde containing systems and such a model can be used to guide more rational design of sol−gel materials.

■ EXPERIMENTAL SECTION

Materials. Formaldehyde stock solution (37 wt %, aqueous solution stabilized by 13 wt % methanol, density 1.08 g/cm^3), tetramethylsilane (TMS, ≥99.9 wt %, NMR grade, ACS reagent), deuterium oxide (99.9 atom % D), benzene (≥99.9 wt %, HPLC grade), and sodium carbonate (≥99.5 wt %, anhydrous ACS reagent) were all purchased from Sigma-Aldrich. Methanol (≥99.8 wt %, ACS grade) was purchased from VWR International LLC. All materials were kept according to specifications provided by suppliers. Measurements of pH of formaldehyde stock solution were carried out throughout and the pH value remained constant at 4.39 ± 0.05. NMR tubes were manufactured by Wilmad (outer diameter, 5 mm; length, 7 in.; limit, 600 MHz), and so were the matching

coaxial inserts (stem length, 50 mm; reference capacity, 60 μL; sample capacity, 530 μL).

Nuclear Magnetic Resonance Spectroscopy. All experiments were performed with a three channel multinuclear Bruker Avance-III 600 MHz instrument, equipped with a 14.1 T Bruker UltraShield magnet and a BBO-z-ATMA-[[31]P-[183]W, ^{1}H] probehead. In order to collect data of quantitative value, full relaxation of all ^{13}C nuclei had to be ensured. Therefore, the T_1 relaxation constants were experimentally established, and the longest was found to be 15 s for the carbon nucleus in methanol.[37] Typically, a 5-fold T_1 value is used as the relaxation delay time between transients. However, a set of preliminary experiments proved that a 60 s long relaxation delay is sufficient to allow for full ^{13}C magnetization recovery. Second, the heteronuclear [13]C-{[1]H} nuclear Overhauser effect was measured, and the results showed the effect to be significant, enhancing some signals by as much as 30%. To eliminate this effect, inverse gated decoupling was applied during the experiments, thereby ensuring that the data were quantitative. Each measurement consisted of 4 dummy scans followed by 1024 scans to provide a good signal-to-noise ratio.

All ^{1}H NMR experiments were performed using the same instrument, however, with a TBI-z-[^{1}H, ^{13}C, [31]P−^{15}N] triple resonance probehead, which is more sensitive toward proton nuclei. No solvent or water suppression was used. Each of the collected spectra comprised of 2 dummy scans followed by 16 scans with relaxation delay time of 1 s. The temperature range of the experiments was 10 to 55 °C at 5 degree increments.

The [^{1}H, ^{13}C] Heteronuclear Single Quantum Coherence (HSQC) method was used to record one-bond correlations between proton and ^{13}C nuclei,[38] so that only protons directly bound to carbon nuclei gave rise to observed NMR responses. With proton being the observed nucleus, relatively short acquisition times were achieved. The main purpose of performing this type of NMR experiment was to accurately assign chemical shifts in both ^{1}H and ^{13}C NMR spectra, especially in the −OH and −CH$_2$− resonance regions. All 2D [^{1}H, ^{13}C] HSQC NMR experiments were performed using the same instrument fitted with a BBO-z-ATMA-[[31]P-[183]W, ^{1}H] probehead. Each spectrum comprised of 16 dummy scans, followed by 4 scans with a relaxation delay time of 4 s. Experiments proved that this number of scans yielded good signal-to-noise ratio. All spectra were collected at 20 °C.

A coaxial insert containing TMS was placed in all samples during experiments at 20 °C (293 K), and benzene, due to its higher boiling point, was used in experiments conducted at elevated temperatures. This was done in order to determine the exact speciation without interference with solution equilibria by

using an internal standard. According to the specifications provided by the manufacturer, the ratio of sample and reference volumes associated with the NMR tube/coaxial insert combination is 530 to 60 μL. This means that the sample signal is 8.83 times greater than that of the reference if the same substance is in both compartments. Experimental verification showed that the actual ratio was 8.94. Therefore, in order to normalize the sample signal, it was divided by this factor during the course of performing calculations. The area of the TMS signal corresponds to four ^{13}C nuclei and to a concentration equal to 7.345 mol·dm^{-3}, while a unit area (U_A) corresponded to one ^{13}C nucleus at a concentration equal to 1 mol·dm^{-3} and was calculated for each spectrum by dividing the area of the TMS signal by its concentration and the number of ^{13}C nuclei. Compositions of investigated solutions are presented in Table 1.

■ RESULTS AND DISCUSSION

Qualitative Analysis of Collected Spectra. In relatively dilute formaldehyde−methanol−water solutions used for the synthesis of formaldehyde based gels, the predominant methylene glycol species are monoglycol (MG), HO−CH$_2$−OH, methoxy monoglycol (MMG), CH$_3$O−CH$_2$−OH, and diglycol (DG), HO−CH$_2$-O−CH$_2$−OH. In addition to these three main species, minor dimeric (methoxy diglycol, MDG, CH$_3$O −CH$_2$−O−CH$_2$−OH) and trimeric (triglycol, TG, HO−CH$_2$−OCH$_2$−OCH$_2$−OH, and methoxy triglycol, MTG, CH$_3$O−CH$_2$−OCH$_2$−OCH$_2$−OH) species were observed.

Examples of typical ^{13}C NMR spectra of formaldehyde solutions investigated in this work are shown in Figure 1. Parts a and b of Figure 1 show spectra for solutions prepared by diluting the formaldehyde stock solution by 1:6 (v/v) with water (F−W 1−6) and methanol (F−MeOH 1−6), respectively. The most prominent resonance observed in the F−W solution (Figure 1a) corresponds to MG, accompanied by signals for MMG, DG and MeOH. On the other hand, the strongest resonance observed in the F−MeOH solution (Figure 1b) corresponds to methanol (as expected), accompanied by signals for MMG. In both cases, small signals corresponding to larger oligomers (e.g., MDG, TG, MTG) can also be observed.

Figure 2 shows details of ^{13}C NMR spectra for the formaldehyde solution F−W 1−3 with the focus being on signals from −CH$_2$− and −CH$_3$− groups where peaks for larger oligomers (MDG, TG, and MTG) can be clearly observed together with small peaks corresponding to small amounts of larger species. It is noted that all ^{13}C NMR spectra were fully quantitative and therefore concentrations of all individual species up to the level of trimers were determined over a range of solution compositions and temperatures.

Analysis of the ^{1}H NMR spectra is more complex than ^{13}C NMR spectra due to the signal resulting from the hydroxyl groups of water, ethanol, and glycols. Moreover, because of high water content and the chemical exchange occurring between proton and deuterium nuclei, the peak was found to be very broad, overlapping signals of the proton nuclei in the −CH$_2$ groups of glycols and methoxyglycols, especially at near ambient temperatures. Examples of ^{1}H NMR spectra for formaldehyde stock solutions diluted with water or methanol are shown in Figure 3.

Although peak suppression techniques (cf. ref 35) may be used in instances when the water peak is sufficiently shifted relative to signals of interest (as it might be at elevated temperatures, see below), this is clearly not the case at 20 °C
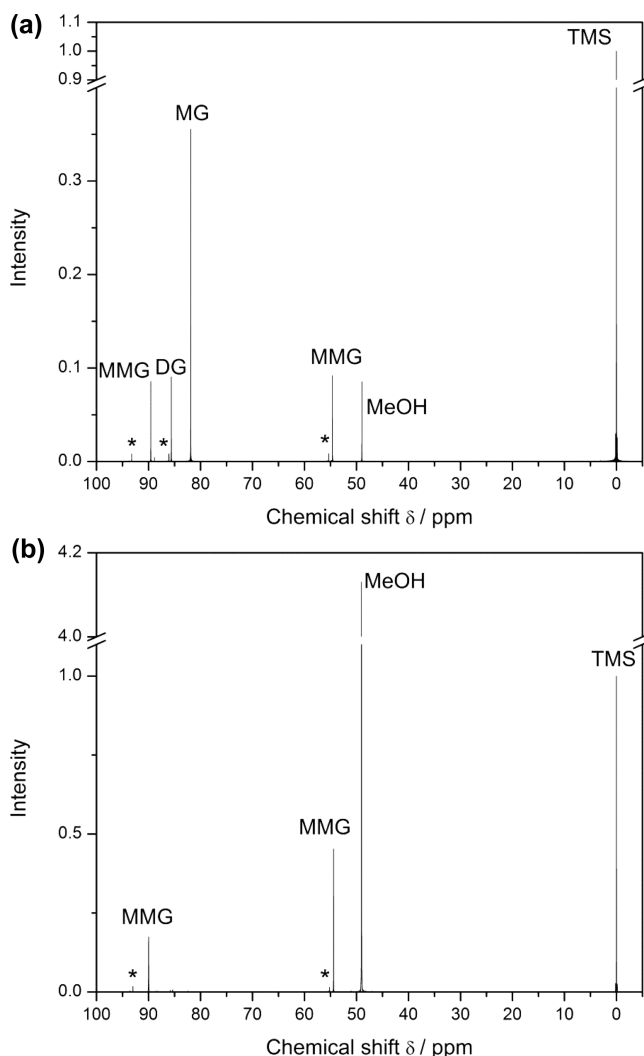

Figure 1. ^{13}C-{^{1}H} NMR spectra of formaldehyde solutions at 20 °C. (a) F−W 1−6, (b) F−MeOH 1−6. Asterisk denotes signals from larger oligomers. All chemical shifts are referenced to TMS ($\delta = 0$).

for the system investigated here. However, even when the peak overlap is extensive, it is possible to carry out deconvolutions for OH and −CH$_2$− signals. All spectra were deconvoluted using Origin 8.1 software, the shape of peaks being assumed as Lorentzian.[38] An example of the effects of deconvolution is shown in Figure 4. While larger peaks (MG, MMG, DG, MDG) can be reasonably well deconvoluted, some minor peaks (e.g., MTG) do not appear in deconvoluted spectra due to difficulties with converging the deconvolution procedure. It is clear that, in order to reliably quantify minor species, the overlap of their peaks with the OH peak should be avoided. This can be accomplished by working at higher or lower temperatures, as discussed further below.

Assignments of signals in ^{13}C and ^{1}H NMR data are reported in previously published literature.[15,33] In order to confirm these assignments, 2D [^{1}H, ^{13}C] HSQC NMR experiments were performed, as along with correlations between calculated and measured chemical shifts (see Supporting Information for further details). The values of chemical shifts are shown in Supporting Information in Table S1 and Table S2. ^{13}C NMR chemical shifts varied relatively little with solvent composition and temperature, while ^{1}H NMR chemical shifts showed much
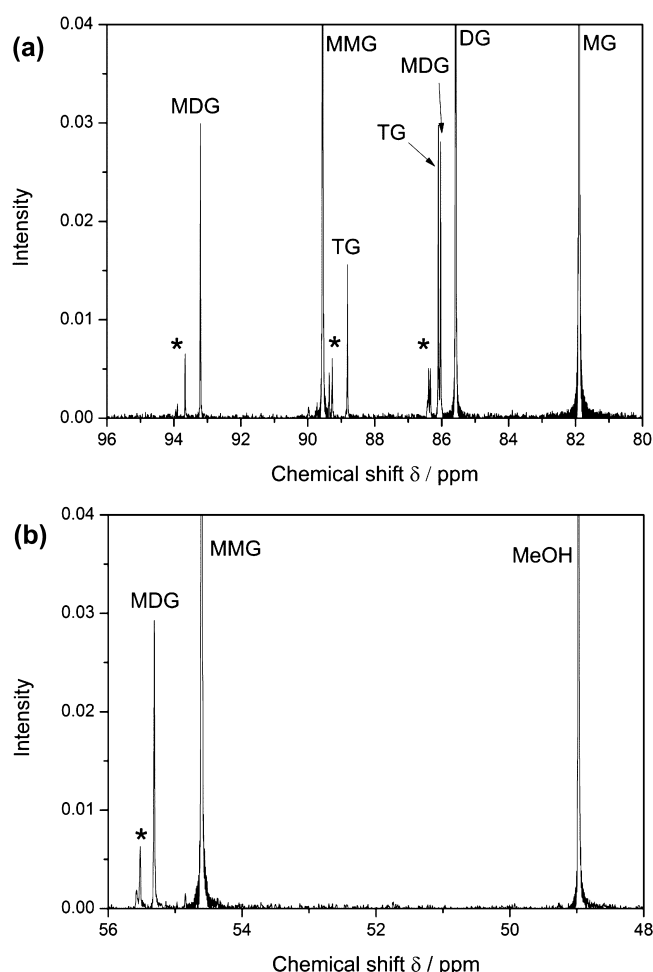
Figure 2. ^{13}C-$\{^{1}H\}$ NMR spectra of formaldehyde solution F−W 1−3 at 20 °C. (a) −CH$_2$− region, (b) −CH$_3$− region. Asterisk denotes signals from MTG species. All chemical shifts are referenced to TMS ($\delta = 0$).

Figure 3. ^{1}H NMR spectra of formaldehyde solutions at 20 °C: (a) F−W 1−6, (b) F−MeOH 1−6. All chemical shifts are referenced to TMS ($\delta = 0$).

stronger dependence on both parameters, as discussed below in further detail.

^{1}H NMR chemical shifts vary with solvent composition, as shown in Figure 5. It is apparent that the −OH peak moves downfield with increasing methanol concentration, that is, with increasing formaldehyde concentration in F−W solutions as well as with formaldehyde concentration in F−MeOH solutions. The influence of methanol and water concentrations is particularly strong on this peak, as it is associated with the hydroxyl groups. These are known to form weak hydrogen bonds and exchange the proton attached to the oxygen atom. This is believed to be the reason for the changes observed. However, chemical shifts of other peaks also move as a function of methanol concentration, while signals for all formaldehyde related species as well as those for methanol itself, change chemical shift approximately equally so their chemical shift differences stay constant.

There is very little information in the previous literature concerning the temperature dependence of the ^{1}H NMR spectra of formaldehyde solutions, even though syntheses involving formaldehyde solutions are often conducted at elevated temperatures. Therefore, a series of ^{1}H NMR experiments were performed over temperatures ranging from 10 to 55 °C. An overlay of three selected spectra from these experiments is shown in Figure 6a. It can be clearly seen that
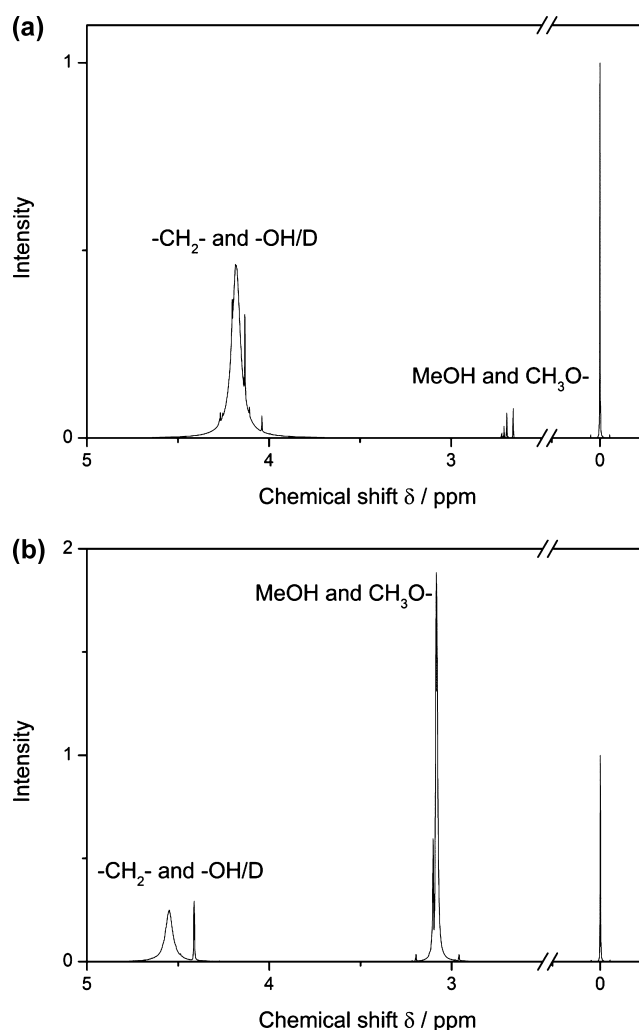
the temperature causes the −OH signal to change chemical shift and sharpen significantly (as expected), while signals corresponding to formaldehyde related species moved considerably less.

The chemical shift of the −OH peak depends linearly on solution temperature, as shown in Figure 6b. The benzene signal was referenced to $\delta^{1}H = 7.0$ ppm. Relative shifts of other signals were then recorded. With increasing temperatures, the −OH peak migrates upfield faster than peaks for other species and so at higher temperatures (above 55 °C) it no longer overlaps with any signals from the −CH$_2$− groups. Conversely, the same should be true for lower temperatures (about 0 °C and below) if the linear relationship in Figure 6b can be extrapolated. The positions of signals for all formaldehyde related species as well as for methanol move approximately equally with temperature so their chemical shift differences stay constant over the temperature range investigated here.

Quantitative Determination of Species Distributions. ^{13}C NMR was used quantitatively to determine concentrations of formaldehyde related species in formaldehyde−water−methanol solutions over a range of compositions and temperatures. In order to validate the method, the total concentrations of formaldehyde and methanol related species measured were first checked to ensure agreement with calculated values. The
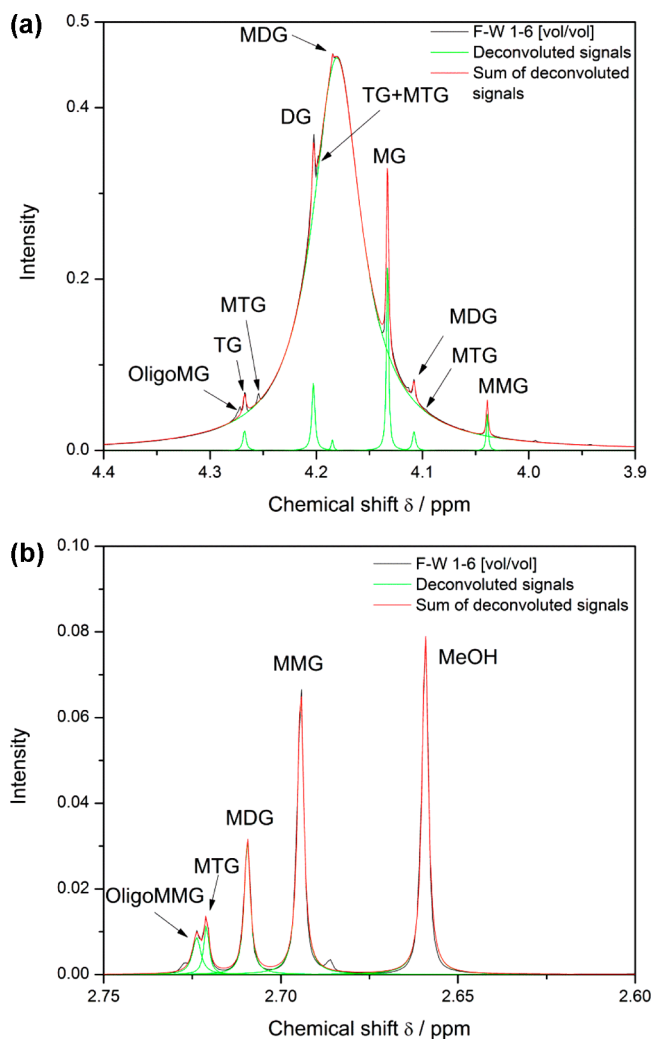
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Figure 4. Deconvolution of ^{1}H NMR spectra of formaldehyde solution F−W 1−6 at 20 °C: (a) −OH/D and −CH$_2$− region, (b) CH$_3$O− region. All chemical shifts are referenced to TMS ($\delta = 0$).

Figure 5. Changes in chemical shift of the (a) −OH/D and (b) MMG peaks in formaldehyde solutions (F−W and F−MeOH) as a function of the total concentration of formaldehyde.

differences were below 6% (with the exception of F-MeOH 1−3, for which values were below 10%), which was considered to be acceptable (see Supporting Information, Tables S3 and S4, for details). Figure 7 shows a comparison of measured and calculated concentrations (which are in good agreement with one another) of all methanol related species, including methanol as well as all methoxylated species and the concentration of free methanol. It can be seen that at higher formaldehyde concentrations, most of the methanol is bound up as methoxylated glycols; as expected, methanol acts as stabilizer in formaldehyde solutions preventing excessive polymerization through formation of methoxyglycols.

Results obtained from ^{13}C NMR allowed the distribution of the six major species present to be described together changes arising from variations in solution composition over a range of water−methanol mixtures. The speciation in the solutions investigated is shown in Figure 8. It is apparent that for both F−W and F−MeOH solutions, oligomeric species become more abundant with increasing formaldehyde concentration as expected. In F−W solutions, total concentrations of both formaldehyde and methanol increase proportionately (since these solutions were prepared by dilution of formaldehyde stock solution with water). Consequently, the proportion of
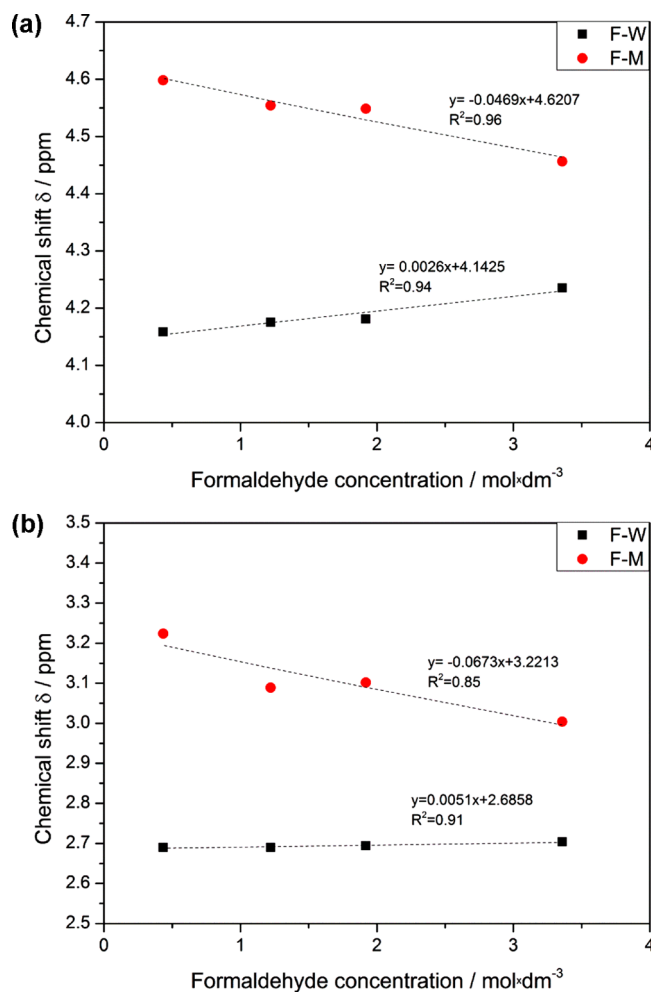
methoxylated monomer (MMG) increases most prominently, while concentrations of dimer (DG), trimer (TG), and their methoxylated forms increase at a slower rate. On the other hand, in F-MeOH solutions the total concentration of methanol decreases with increasing total formaldehyde concentration (since these solutions were prepared by dilution of formaldehyde stock solution with methanol). Thus, the proportion of MG increases at the expense of MMG as the methanol concentration decreases with increasing total formaldehyde concentration. In addition, concentrations of DG and MDG increase with increasing total formaldehyde concentration as expected.

Figure 8 also shows curves corresponding to calculated values of molar fractions of total formaldehyde present in the form of respective species from the equilibrium speciation model using average values of equilibrium constants from Table 3 (see further discussion).

Oligomerization and Methoxylation Equilibrium Constants. The main purpose of ^{13}C NMR measurements was to achieve quantitative determination of the speciation in formaldehyde solutions over a range of water−methanol mixtures. This information can now be used to calculate equilibrium constants of oligomerization and methoxylation in these solutions (see Table 2), using directly measured concentrations of relevant species involved in respective
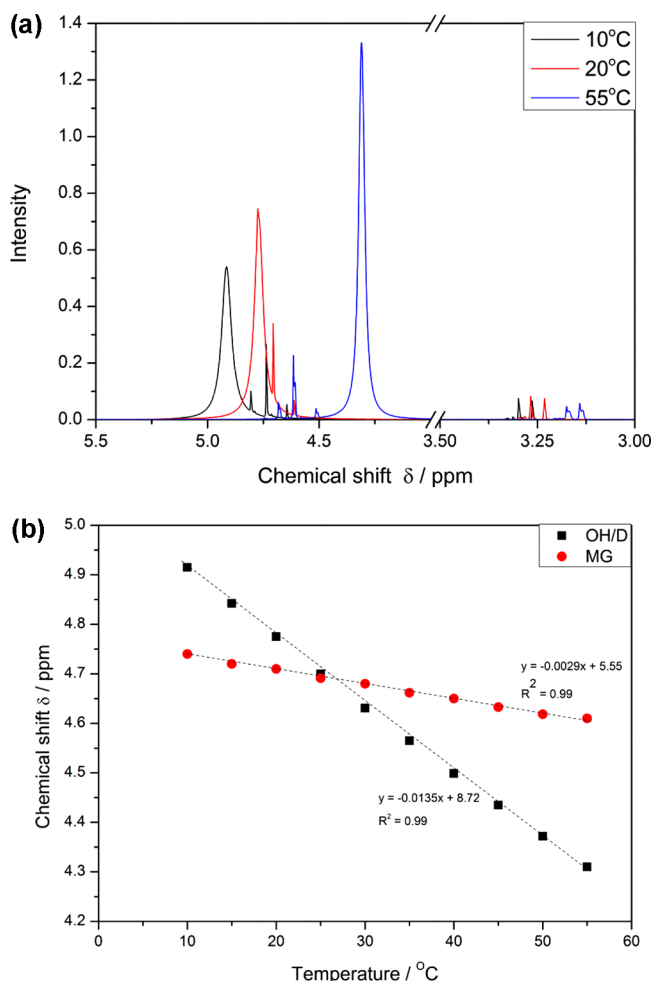
Figure 6. (a) Example of ^{1}H NMR spectra of formaldehyde solutions (F−W 1−6) at three different temperatures All chemical shifts are referenced to benzene ($\delta = 7$). (b) Changes of chemical shift of −OH and MG (HO−C$\underline{H}_2$−OH) peaks between 10 to 55 °C.
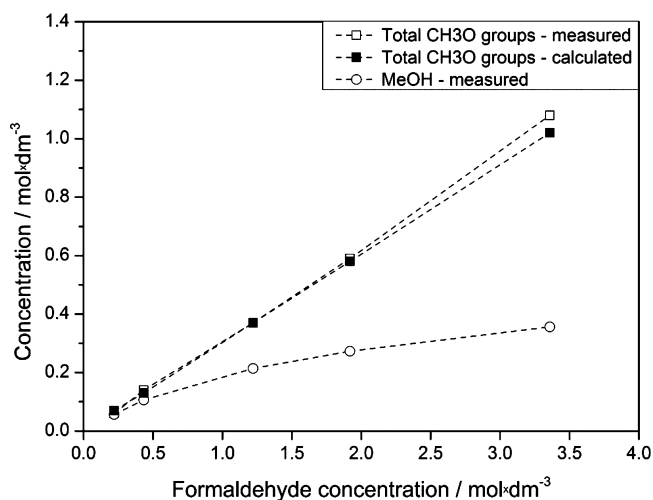

Figure 7. Comparison of measured and calculated concentrations of total methanol related species and free methanol in formaldehyde solutions F−W (1−3, 1−6, 1−10, 1−30, 1−60) as a function of the total concentration of formaldehyde.

reactions (see Table S5 in Supporting Information). These equilibrium constants can then be used for predicting
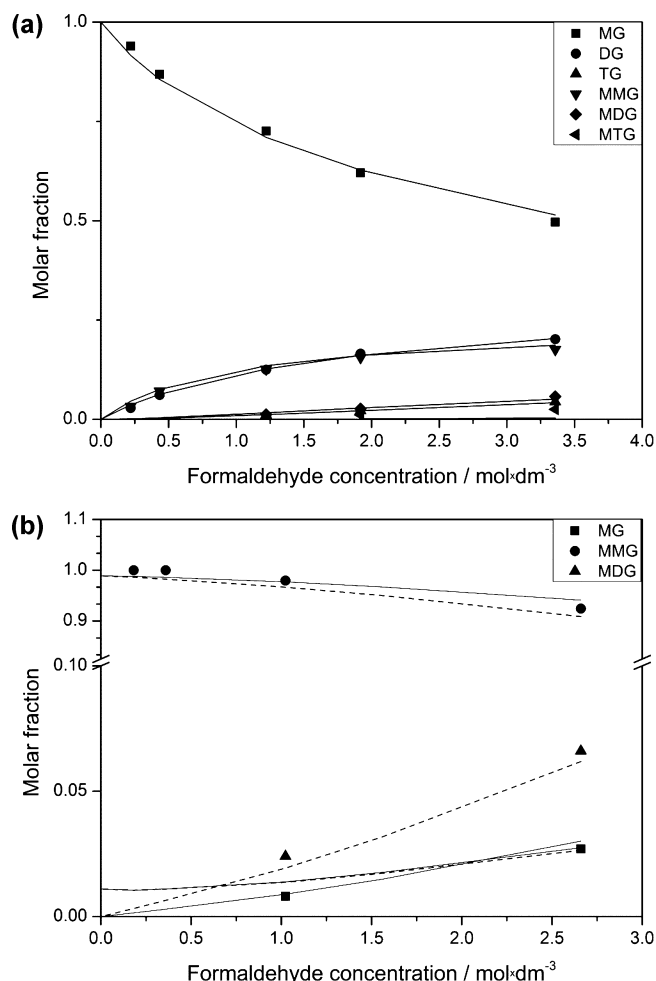

Figure 8. Species distribution in formaldehyde solutions expressed in terms of molar fractions of total formaldehyde as a function of the total concentration of formaldehyde, measured by ^{13}C NMR at 20 °C: (a) F−W solutions, (b) F−MeOH solutions. Solid lines correspond to values calculated from the equilibrium speciation model using average values of equilibrium constants from Table 3. Dashed lines correspond to values calculated with $K_1 = 12$ (see text).

Table 2. Reactions of Formaldehyde-Related Species in Water−Methanol Solutions with Their Concentration Equilibrium Constants

reaction	equilibrium constant
MG + MG = DG + H$_2$O	$K_1 = [DG][H_2O]/[MG]^2$
MG + MeOH = MMG + H$_2$O	$K_2 = [MMG][H_2O]/[MG][MeOH]$
DG + MG = TG + H$_2$O	$K_3 = [TG][H_2O]/[MG][DG]$
DG + MeOH = MDG + H$_2$O	$K_4 = [MDG][H_2O]/[DG][MeOH]$
TG + MeOH = MTG + H$_2$O	$K_5 = [MTG][H_2O]/[TG][MeOH]$

speciation in formaldehyde solutions at other compositions and temperatures (see Supporting Information for further details). Table 2 shows the definitions of relevant equilibrium constants based on molar concentrations. It is noted that all concentration based equilibrium constants shown here have the same values as those based on molar fractions.

We are not aware of any previous work by other authors that provide values of methoxylation equilibrium constants (K_2 or K_4) in mixed solvent methanol−water solutions. However, Hahnenstein et al. have reported in their work values of

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Table 3. Equilibrium Constants Calculated Using Concentrations Measured by ^{13}C NMR at 20 °C (see Table S5 in Supporting Information).[a]

	F−W solutions					
equilibrium constant	1−3	1−6	1−10	1−30	1−60	avg. value
K_1	5.76 (4.05)	5.72 (4.44)	5.15 (4.25)	5.15 (4.72)	4.23[†] (4.03[†])[b]	5.45 (4.37)
K_2	46.8 (41.3)	46.4 (41.4)	42.5 (38.6)	41.7 (39.7)	33.5[†] (32.6[†])	44.4 (40.3)
K_3	4.11 (3.58)	3.74 (3.38)	3.43[†] (3.17[†])			3.93 (3.48)
K_4	37.4 (46.7)	29.8 (33.8)	24.1[†] (26.1[†])			33.6 (40.3)
K_5	11.1 (12.1)	8.39[†] (8.71[†])				11.1 (12.1)
K_m	0.098 (0.111)	0.079 (0.087)	0.069[†] (0.074[†])			0.089 (0.099)

[a]Values of equilibrium constants corrected with activitiy coefficients are shown in parentheses. Free water concentration $[H_2O]$ was calculated as water added ($H_2O + D_2O$) + water from formaldehyde stock solution: MG−DG−TG. [b][†] values not used to calculate average value, as they are subject to larger uncertainty, since relevant species concentrations were below 0.01 M.

equilibrium constants for MMG dimerization in purely methanolic solutions:

$$CH_3O-CH_2-OH + CH_3O-CH_2-OH$$
$$= CH_3O-CH_2-O-CH_2-OH + CH_3OH$$
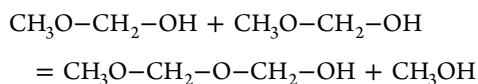
$$K_m = [CH_3O-CH_2-O-CH_2-OH][CH_3OH]$$
$$/[CH_3O-CH_2-OH]^2$$

Note that it is also possible to express K_m in terms of other equilibrium constants as follows: $K_m = K_1 K_4/K_2^2$.

The values of equilibrium constants were directly calculated from concentrations of relevant species measured in formaldehyde solutions using ^{13}C NMR, and the results are shown in Table 3. We note that there was no data fitting involved in determination of equilibrium constants, since we measured concentrations of all species involved except that of (free) water, which was calculated from the corresponding material balance, as shown in Table S5 (see Supporting Information).

The equilibrium constant values shown in Table 3 indicate that MG and oligooxyglycols are more susceptible to reacting with methanol and forming methoxylated forms like MMG, MGD, and MTG rather than forming longer oligooxyglycols. Values of equilibrium constants for these reactions are 44.3, 30.4, and 9.74, respectively, while equilibrium constants of DG and TG formation are smaller by an order of magnitude, equal to 5.43 and 3.76, respectively. This is consistent with the role of methanol, which is present in the commercially available formaldehyde solutions as a stabilizing agent to prevent polymerization of methylene glycol. Since no detectable amount of formaldehyde in the aldehyde form was found, it was impossible to estimate the equilibrium constant for MG formation using our experimental data. Previous investigations showed that this equilibrium constant has a very high value of around 2000 under ambient conditions[5] so that expected concentartions of free formaldehyde in solutions investigated would be expected to be very low.

It can be seen in Table 3 that there appears to be a consistent trend with all equilibrium constants decreasing with increasing dilution of the formaldehyde stock solutions. In general, the solutions are not actually ideal, and some of the concentration dependence of the equilibrium constants can be attributed to the nonideal mixing of the components in the system. The variation of the activity coefficients of the species in the solution were estimated using the UNIFAC model,[39] with the molecular size, surface, and interaction parameters taken from previously published literature . The "corrected" equilibrium constants are given in parentheses in Table S5, Supporting

Information. Note that, for these corrections, the asymmetric convention is taken, where the activity coefficients of the solute species approach unity in the limit of infinite dilution (i.e., the solution approaches pure solvent). However, as can be seen in Figure 8a, using average values for concentration based equilibrium constants over the range of concentrations covered in F−W solutions (see Table 3), accurate prediction of speciation in these solutions is achieved.

Using the same set of equilibrium constants in the calculation of speciation in F−MeOH solutions, however, results in less accurate predictions (see solid lines in Figure 8b). It can be estimated from measured species concentrations in these solutions (see Table S6 in Supporting Information) that corresponding equilibrium constants K_m must be significantly higher, with values around 0.2, than those determined in F−W solutions. Although it was not possible to estimate further constants accurately due to limited data available, it turned out that it is sufficient to adjust the dimerization equilibrium constant K_1 to 12 in order to obtain much improved agreement between experimental and modeling results (see Figure 8b). Regardless of this, it is clear that some of the equilibrium constants determined for low methanol solutions (F−W samples) would need to be modified in order to achieve quantitatively accurate predictions of species distribution in predominantly methanolic solutions.

Estimated equilibrium constants determined in this work can be compared with those obtained by Hahnenstein et al.[13] In their work, ^1H and ^{13}C NMR spectroscopy was used to investigate solutions of formaldehyde in either water, D_2O, or methanolic solutions prepared by depolymerization of paraformaldehyde in pure solvents. The resulting molar fraction of total formaldehyde was considerably higher than those used in our work. Equilibrium constants determined by Hahnenstein et al. in purely aqueous solutions at 20 °C equivalent to our K_1 (their K_{HF2}) and K_3 (their K_{HFn}) were 6.77 and 4.20, respectively. Moedritzer and Van Wazer reported estimated an equilibrium constant equivalent to our K_1 to be equal to 4 in purely aqueous solutions.[17] These previously published values are similar to those determined in this work (see Table 3). The values of K_m reported by Hahnenstein et al. were 0.144 and 0.127 (determined by ^1H NMR and ^{13}C NMR, respectively) for purely methanolic solutions without any added water at 20 °C. Balashov et al. reported similar values in highly methanolic solutions. Corresponding values of K_m determined here for more dilute, predominantly aqueous solutions were somewhat lower, with values below 0.1 (see Table 3). However, equilibrium constants K_m estimated from species distributions measured in predominantly methanolic solutions (F−MeOH

samples) investigated here were significantly higher, with values around 0.2.

Additional experiments were performed over a range of temperatures from 10 to 55 °C (with 5 °C increments) in order to investigate dependency of equilibrium constants on temperature. Equilibrium constants were calculated as described previously, using the concentrations of form-aldehyde-related species and methanol measured by ^{13}C NMR and the concentration of free water calculated as shown above. Resulting values are shown in Figure 9. Activity
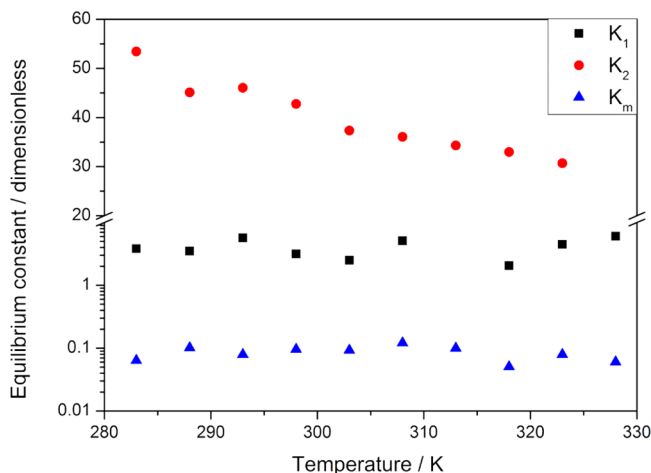

Figure 9. Equilibrium constants K_1, K_2, and K_m vs temperature for F–W 1–6 solutions.

coefficient correction factors for the equilibrium constants shown in Figure 9 were found to be relatively independent from temperature and are shown in Table S8, Supporting Information.

The equilibrium constants of DG and MDG formation through MG and MMG dimerization (K_1 and K_m), respectively, do not show any significant trend with temperature, while the equilibrium constant of MMG formation through MG methoxylation (K_2) decreases with increasing temperature. Temperature dependence of equilibrium constants K_1 (their K_{HF2}) and K_m in purely aqueous and purely methanolic solutions, respectively, was reported previously:[15] K_1 was found to slightly decrease with temperature between 10 and 80 °C, while K_m was found to slightly increase with temperature. However, in our system there seemed to be no strong temperature dependence for either equilibrium constant, while it was noted that the solution matrix was significantly different from that used in other studies.

CONCLUSIONS

In this work, the distributions of formaldehyde related species in moderately concentrated formaldehyde−methanol−water solutions have been quantitatively determined over a range of solution compositions and temperatures. ^{13}C NMR spectros-copy was used for quantitative determination of formaldehyde related species and while ^{1}H NMR can also be used to quantitatively monitor all species present, the overlap of a broad −OH peak with signals from −CH$_2$− groups presents a problem at ambient temperatures. However, since ^{1}H NMR chemical shifts move significantly with temperature, working at sufficiently lower (0 °C or less) or higher (55 °C or more) temperatures allows spectra to be obtained that are clear of

such overlap. 2D [^{1}H, ^{13}C] HSQC NMR experiments were also used to confirm assignments of relevant chemical shifts in ^{1}H and ^{13}C spectra.

Concentrations of small methylene glycol oligomers and their methoxylated forms found in these solutions were measured over a range of formaldehyde concentrations and methanol−water ratios and at temperatures between 10 and 55 °C. Based on these results, equilibrium constants for methylene glycol dimer and trimer formation as well as for methoxylation of these oligomers were calculated using measured concen-tration values. The methoxylation equilibrium constants K_2 and K_4 were much larger than oligomerization constants, which explains why the presence of methanol favors formation of methoxylated species and shifts the overall speciation equilibrium toward smaller species and limits formation of larger oligomers. The methoxylation equilibrium constant K_2 was found to decrease with temperature, while the dimerization equilibrium constant K_1 was essentially independent of temperature over the range of conditions investigated.

Accurate knowledge of equilibrium constants of oligomeriza-tion and methoxylation reactions in mixed aqueous−methanolic solutions allows quantitative prediction to be made of speciation in formaldehyde solutions used for the synthesis of organic gels and can be used for more rational design of formaldehyde based sol−gel processes.

ASSOCIATED CONTENT

S Supporting Information

Results and interpretation of [^{1}H, ^{13}C] HSQC experiments, correlations between calculated and measured chemical shifts, qualitative validation of ^{13}C NMR spectra integration and species distribution determination, as well as activity coefficient correction factors for the equilibrium constants shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

DEDICATION

We dedicate this paper to Prof. Massimo Morbidelli in recognition of his outstanding contributions to the field of chemical engineering on the occasion of his 60th birthday.

ABBREVIATIONS

MG = monoglycol (HO−CH$_2$−OH)
MMG = methoxy monoglycol (CH$_3$O−CH$_2$−OH)
DG = diglycol (HO−CH$_2$−O−CH$_2$−OH)
MDG = methoxy diglycol (CH$_3$O−CH$_2$−O−CH$_2$−OH)
TG = triglycol (HO−CH$_2$−O−CH$_2$−O−CH$_2$−OH)
MTG = methoxy triglycol (CH$_3$O−CH$_2$−O−CH$_2$−O−CH$_2$−OH)

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