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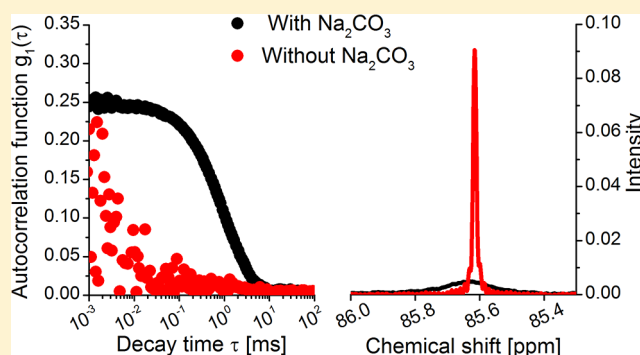
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Molecular Speciation and Mesoscale Clustering in Formaldehyde–Methanol–Water Solutions in the Presence of Sodium Carbonate

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ABSTRACT: Nanoporous organic gels can be synthesized from aqueous solutions of formaldehyde and resorcinol in the presence of basic electrolytes such as sodium carbonate. It is well known that formaldehyde is present in the form of methylene glycols or methoxy-glycols in aqueous and methanolic solutions, but influence of pH or electrolytes on speciation in these solutions has not been previously studied. Here we investigated effects of sodium carbonate on the speciation and colloidal scale clustering in formaldehyde–methanol–water solutions in the absence of resorcinol. We used ^{13}C NMR spectroscopy to quantitatively characterize molecular speciation in solutions and to estimate corresponding equilibrium constants for glycol dimerization and methoxylation. We found that species distribution is essentially independent of carbonate concentration for pH values between 3.4 (no carbonate) and 10.6. This was also consistent with ATR IR measurements of the same solutions. However, NMR spin–spin relaxation time measurements showed an unexpected behavior for glycols and especially for diglycol (but not for methanol), with relaxation times strongly decreasing with increasing carbonate concentration, indicating differences in local molecular environment of glycols. We further used dynamic light scattering to confirm the presence of mesoscale clustering in formaldehyde–methanol–water (for both H_2O and D_2O) solutions in the presence of sodium carbonate. We propose that the observed phenomena are due to glycol-rich cluster mesospecies in equilibrium bulk solution, together forming a thermodynamically stable mesostructured liquid phase.



■ INTRODUCTION

Formaldehyde-based resins and gels are typically synthesized from aqueous solutions of formaldehyde and reactants such as phenol, resorcinol, melamine, or urea, which react with formaldehyde and undergo subsequent polymerization.¹ Formaldehyde substitution as well as further polymerization is catalyzed by both acids and bases, and so the kinetics of resin and gel formation are dependent on pH. Furthermore, the microstructure of resulting gels is dependent on solution pH as well as on the nature of the ions involved.^{2,3}

Formaldehyde in aqueous solutions is present in its hydrated form as methylene glycol, which is prone to polymerization unless methanol is added to promote the formation of methoxyglycols (MMGs), which stabilizes small oligomers at the expense of polymerization. The nature of aqueous and methanolic solutions of formaldehyde was previously examined using gas chromatography and ^1H and ^{13}C NMR spectroscopy, and equilibria between glycol oligomers present in solutions were quantified.^{4–8} Formaldehyde solutions were usually prepared by dissolution of poly(oxymethylene) in either water or methanol, but very few studies^{9,10} were concerned with mixed water–methanol solvents such as those in commercially available formaldehyde solutions and typically

used for the preparation of formaldehyde-based resins and gels. Hahnenstein et al.⁴ focused on speciation of formaldehyde in water, deuterium oxide, and methanol, providing values of glycol condensation equilibrium constants in aqueous solutions (with no methanol) and MMG condensation equilibrium constants in methanolic solutions (with no water). Balashov et al.⁹ focused on speciation of formaldehyde in highly concentrated alcoholic (methanol, ethanol, ethylene glycol) solutions at relatively low water concentrations, providing values of MMG condensation equilibrium constants in methanolic solutions. A study by Maiwald et al.¹⁰ provided further NMR spectra assignments by performing 2D heteronuclear ^1H – ^{13}C correlation experiments. However, methoxylation equilibrium constants for methylene glycol species have not been explicitly determined in previous studies, and effects of solution pH and electrolyte concentration have not been investigated, although these are well known to influence both kinetics and microstructure of resulting formaldehyde based gels. To assess the role of solution pH

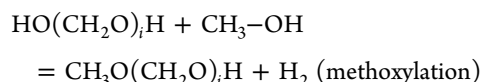
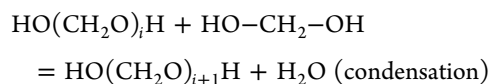
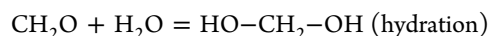
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and electrolyte concentration in this context, we set out to investigate the effect of sodium carbonate, which is commonly used in the preparation of resorcinol–formaldehyde gels.

Speciation of formaldehyde (CH_2O) in aqueous solutions in the presence of methanol can be represented by the following general equations:^{11–13}



The first reaction has a high equilibrium constant under ambient conditions¹³ so that there is only a very low concentration of free formaldehyde present in aqueous solutions under typical conditions used in synthesis of formaldehyde based gels. Because all formaldehyde-related species as well as methanol and water are involved in mutual equilibria, their relative proportions are dependent on the total formaldehyde and methanol concentrations in the solution.

While water, methanol, and methylene glycols appear to be mutually miscible over a wide range of concentrations and temperatures, the effect of electrolytes on speciation and equilibria in these solutions has not been previously investigated. It is well known that the presence of electrolytes can lead to macroscopic phase separation in water–alcohol mixtures and mesostructured liquid phases have been observed in aqueous solutions of zwitterions and other well-soluble solutes. Furthermore, alcohols are subject to protonation/deprotonation equilibria with changing pH, which can promote molecular as well as mesoscale clustering in aqueous solutions. We have also recently reported on thermodynamically controlled formation of nanoscale primary clusters in polymerizing resorcinol–formaldehyde solutions in the presence of sodium carbonate.¹⁴ We investigate speciation and mesoscale clustering in aqueous–methanolic solutions of formaldehyde using nuclear magnetic resonance spectroscopy, infrared spectroscopy, and dynamic light scattering (DLS) to elucidate the effects of electrolyte concentration and pH on molecular speciation and microscopic phase behavior of these solutions, which are precursors for the synthesis of many promising organic gel based materials.

■ EXPERIMENTAL SECTION

Formaldehyde stock solution (37 wt %, aqueous solution stabilized by 13 wt % methanol; the concentration of methanol was determined using ^{13}C NMR spectroscopy¹⁵), tetramethylsilane (TMS, $\geq 99.9\%$ wt., NMR grade, ACS reagent), deuterium oxide (99.9 atom % D), and sodium carbonate (≥ 99.5 wt %, anhydrous ACS reagent) were all purchased from Sigma-Aldrich. Syringe filters (0.02 μm pore size, Anotop 10; manufactured by Whatman) were purchased from Fisher Scientific. Filtration was carried out with rubber-free PVC/PP syringes. Cylindrical vials for DLS experiments were made from borosilicate glass, with diameter 10 mm and height 75 mm, and were also purchased from Fisher Scientific.

Compositions of investigated solutions were chosen to be similar to those typically used in the synthesis of formaldehyde–resorcinol gels.^{1,2} Although no resorcinol was used here, these

compositions would correspond to resorcinol to water and resorcinol to formaldehyde ratios equal to 0.10 g/mL and 0.5 mol/mol, respectively, while amounts of sodium carbonate (often described as catalyst) would correspond to resorcinol to catalyst ratios 50, 100, 200, and 500 mol/mol and no catalyst for samples 5, 4, 3, 2 and 1, respectively. The actual concentrations of sodium carbonate were 0.0152, 0.0076, 0.0038, 0.0015, and 0 mol $\cdot\text{dm}^{-3}$ for samples 5, 4, 3, 2 and 1, respectively. Water (H_2O) was used as a solvent for IR experiments; a mixture of H_2O and D_2O at a volumetric ratio of 7 to 3 was used for NMR experiments, and both pure H_2O and a mixture of H_2O and D_2O were used for DLS experiments.

The required mass of sodium carbonate and 10 mL of solvent were mixed together in a glass beaker for 5 min using a magnetic stirrer; then, 1.47 mL of formaldehyde stock solution was added. After an additional 15 min of stirring, samples of solutions were drawn for experiments. All samples were kept at 20 $^\circ\text{C}$, and all measurements were performed at this temperature.

The pH was measured using a single reference (Ag/AgCl) glass electrode (Hanna Instruments, model pH 20), suitable for measurements in the presence of alcohols. All pH measurements were taken prior to further experiments (NMR, IR, DLS).

NMR experiments were performed using a three-channel multinuclear Bruker Avance-III 600 MHz NMR spectrometer, equipped with a 14.1 T Bruker UltraShield magnet and a TBI-z- $[\text{}^1\text{H}, \text{}^{13}\text{C}, \text{}^{31}\text{P}-\text{}^{15}\text{N}]$ probehead. To ensure full relaxation of ^{13}C nuclei and thus allow quantitative measurements, appropriately long relaxation delay times were used. Spin–lattice relaxation time constants, T_1 , were determined and because the longest measured time was 15 s (for methanol), a delay time of 60 s was used.¹⁵ Additionally, inverse-gated decoupling was applied to eliminate the nuclear Overhauser effect. Each experiment consisted of 1024 scans to provide a good signal-to-noise ratio, and a coaxial insert with TMS was used for reference. According to the volume specifications provided by the manufacturer, the NMR signal of the substance in the sample compartment should be 8.833 times greater than that of the same substance in the coaxial insert. Experimental validation showed that the actual ratio was 8.943, and this was used when determining absolute concentrations of species in investigated samples.

IR spectroscopic experiments were performed using a MB3000 mid-IR Fourier transform spectrometer manufactured by ABB equipped with class 3B laser (760 nm, 2 mW output power) and an ATR (attenuated total reflection) probe linked by an optical fiber cable. The ATR probe was immersed in each sample measured. All measurements were performed with the same set of parameters: 16 scans, resolution 8 cm^{-1} , using deionized water as a background.

In DLS experiments autocorrelation functions $g_1(\tau)$ were measured using a digital correlator (ALV/LSE-5004 Light Scattering Electronics and Multiple Tau Digital Correlator manufactured by ALV-GmbH). The wavelength λ of incident laser light was 632.8 nm, and the scattering angle θ was set to 90 $^\circ$. The initial decay rate Γ of measured autocorrelation functions $g_1(\tau)$ was estimated using the cumulant method, and the corresponding intensity averaged mean diffusion coefficient D was determined. From this the mean hydrodynamic radius R_h was calculated using the Stokes–Einstein equation.¹⁶ To eliminate dust and any solid particles from samples for DLS experiments, solutions of sodium carbonate in water and

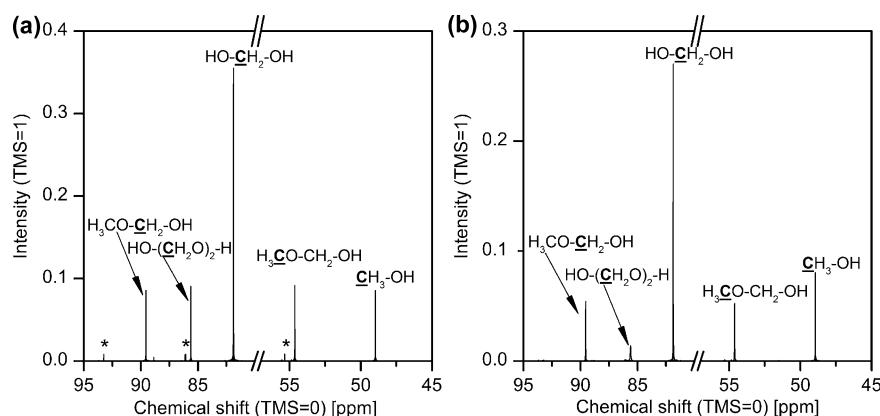


Figure 1. ^{13}C NMR spectrum of formaldehyde–methanol–water–sodium carbonate solutions: (a) sample 1, no sodium carbonate, the asterisk indicates signals from minor oligomeric species (see text) and (b) sample 3, sodium carbonate concentration $0.0038\text{ mol dm}^{-3}$.

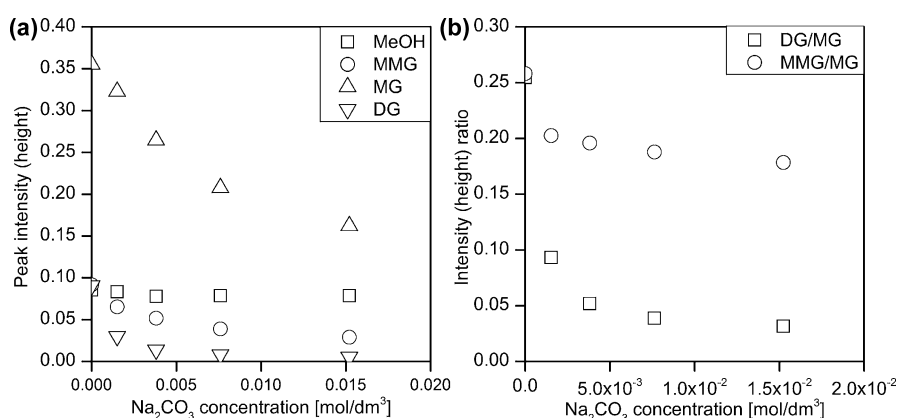


Figure 2. Effect of sodium carbonate concentration on ^{13}C NMR peak intensities (heights): (a) methanol and formaldehyde-related species and (b) ratios of peak intensities (heights) of MMG and DG to that of MG.

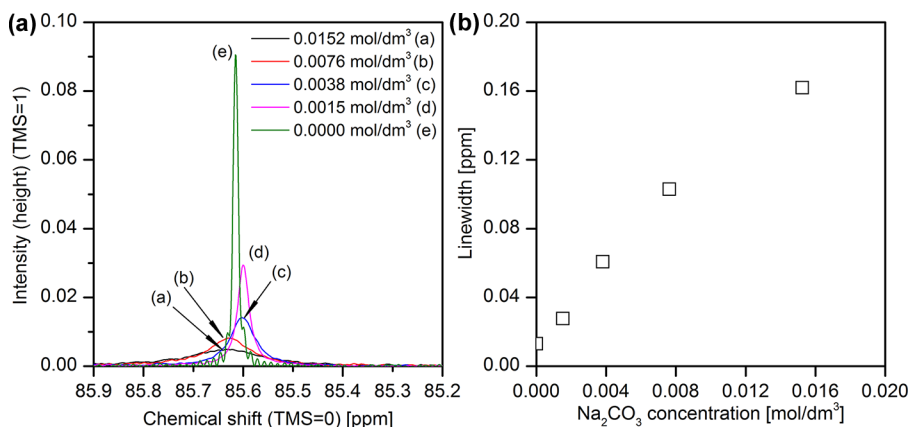


Figure 3. DG signal in ^{13}C NMR spectra of formaldehyde–methanol–water–sodium carbonate solutions: (a) expanded area of spectrum showing DG signal for various sodium carbonate concentrations and (b) effect of sodium carbonate concentration on DG signal peak line width.

formaldehyde stock solution were filtered individually using $0.02\text{ }\mu\text{m}$ syringe filters and mixed together after filtration, followed by stirring for 15 min. DLS experiments were performed for solutions prepared with both H_2O and D_2O to assess the effects of using D_2O as the NMR locking agent.

RESULTS AND DISCUSSION

In relatively dilute formaldehyde–methanol–water solutions used for synthesis of formaldehyde-based gels, predominant methylene glycol species are monoglycol (MG), $\text{HO}-\text{CH}_2-$

OH ; methoxy monoglycol (MMG), $\text{CH}_3\text{O}-\text{CH}_2-\text{OH}$; and diglycol (DG), $\text{HO}-\text{CH}_2-\text{O}-\text{CH}_2-\text{OH}$. In addition to these three main species, minor dimeric (methoxy diglycol, MDG) and trimeric (triglycol, TG; methoxy triglycol, MTG) species were observed by ^{13}C NMR in the sample without sodium carbonate, where their total concentration accounted for $\sim 5\%$ of the total formaldehyde present. However, in the presence of sodium carbonate these minor species were not quantitatively recorded. In Figure 1 we show typical ^{13}C NMR spectra measured in formaldehyde–methanol–water solutions with

Table 1. Comparison of Concentrations (A), Chemical Shifts (B), and Measured pH Values (C) in Formaldehyde–Methanol–Water–Sodium Carbonate Solutions

sample	5	4	3	2	1
Na ₂ CO ₃ concentration [mol•dm ⁻³]	0.0152	0.0076	0.0038	0.0015	0
A					
species	concentration [mol•dm ⁻³]				
MeOH (CH ₃ OH)	0.254	0.266	0.261	0.254	0.273
MMG (CH ₃ OCH ₂ OH)	0.253	0.249	0.264	0.238	0.295
MG (HOCH ₂ OH)	1.09	1.10	1.13	1.09	1.18
DG (HOCH ₂ OCH ₂ OH)	0.129	0.129	0.133	0.128	0.157
total formaldehyde	1.60	1.60	1.66	1.59	1.79
total methanol	0.507	0.515	0.525	0.492	0.568
free water ^a	50.9	50.9	50.8	50.9	50.7
B					
NMR signals	chemical shift [ppm]				
TMS	0.00	0.00	0.00	0.00	0.00
MeOH (CH ₃ OH)	48.96	48.96	48.95	48.95	48.96
MMG (CH ₃ OCH ₂ OH)	54.61	54.62	54.60	54.60	54.61
MG (HOCH ₂ OH)	81.88	81.88	81.86	81.86	81.88
DG (HOCH ₂ OCH ₂ OH)	85.63	85.63	85.60	85.60	85.62
C					
measured pH	10.56	10.38	10.08	9.69	3.37

^aCalculated as: free water = water added (H₂O and D₂O) + water from formaldehyde solution – MG – DG.

and without sodium carbonate. The assignment of peaks corresponding to specific carbon nuclei was based on previous work.^{4,8,15}

As the concentration of sodium carbonate increases, the peak heights of formaldehyde-related peaks gradually decrease, as shown in Figure 2a. Meanwhile, the methanol peak height decreases slightly and then remains approximately constant with changing sodium carbonate concentration. The ratio of peak heights of MG and MMG peaks decreases by a factor of about two, while the DG peak height decreases about 20-fold as the concentration of sodium carbonate increases.

This difference is illustrated in Figure 2b, where the ratio of peak heights of DG to MG changes much more significantly than that of MMG to MG with increasing carbonate concentration. A closer inspection of the NMR spectra revealed that the width of the peaks also varied with increasing carbonate concentration, and this was most prominently the case for DG, as shown in Figure 3.

Line broadening observed here is unlikely to be due to magnetic field inhomogeneity because TMS and methanol peaks are not subject to the broadening observed for formaldehyde-related species. It is also unlikely to be due to chemical exchange between major species: while the methoxy carbon signal from MMG (at 54.6 ppm) broadens by about a factor of 2 with increasing carbonate concentration, the corresponding methanol carbon signal does not broaden. Additionally, their chemical shift difference does not change with carbonate concentration. (See Table 1.) While MG and DG peaks are both subject to broadening, their chemical shift difference does not change either. Another possible source of chemical exchange could be due to deprotonation of hydroxy groups in glycols. The degree of deprotonation is expected to increase with increasing carbonate concentration as pH increases (Table 1), but because the pK_a for MG is ~13.5,¹⁷ at the higher carbonate concentration used here (where the pH is around 10.5), only 0.1% of the total amount of MG is

expected to be deprotonated, and the proton exchange is likely to be very fast, resulting in no peak broadening.

Therefore, it is reasonable to assume that the peak broadening is primarily due to changes in the local environment of molecules, reflected by the spin–spin relaxation time, T_2 . The spin–spin relaxation time can then be estimated from measurements of the line width (LW) of the peak observed in the NMR spectrum using the following equation: $LW = (\pi T_2)^{-1}$.^{18,19} The results of this analysis are shown in Figure 4.

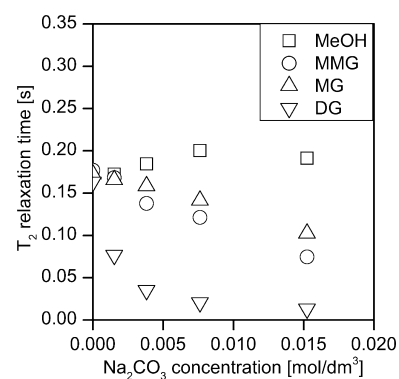


Figure 4. Effect of sodium carbonate concentration on estimated spin–spin–lattice relaxation times, T_2 , for methanol and formaldehyde-related species based on their peak linewidths.

It can be clearly seen that the spin–spin relaxation times decrease significantly for all formaldehyde-related species, while it remains approximately constant for methanol. The most pronounced decrease is observed for DG species: the value of T_2 in the absence of sodium carbonate is ~0.16 s, similar to that of methanol, while in the solution containing the highest concentration of sodium carbonate (0.0152 mol•dm⁻³), the value of T_2 is ~0.013 s. We propose that this is due to the formation of clusters of MG, MMG, and DG molecules, which

Table 2. Comparison of Equilibrium Constants K_1 and K_2 for Formaldehyde–Methanol–Water Solutions with Different Concentrations of Sodium Carbonate

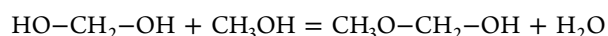
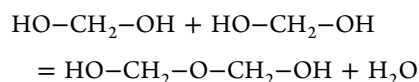
sample	1	2	3	4	5	average
Na ₂ CO ₃ concentration [mol/dm ³]	0	0.0015	0.0038	0.0076	0.0152	0.0015–0.0152
K_1	5.77	5.47	5.26	5.47	5.56	5.44
K_2	45.5	43.5	45.4	43.3	46.7	44.7

is favorable under basic conditions in the presence of sodium carbonate. The mobility of glycols in these clusters is somewhat restricted compared with the surrounding bulk solution, leading to slower tumbling and hence peak broadening.²⁰ We also used DLS to further investigate clusters implied here as discussed below. These clusters are in mutual equilibrium with the surrounding solution, forming a single microscopically heterogeneous liquid phase. Similar behavior has been observed in the early stages of resorcinol–formaldehyde polymerization at 55 and 80 °C using DLS, where clusters with diameters of several nanometers were observed,¹⁴ and also in aqueous solutions of amino acids (e.g., glycine), where DLS, SAXS, and Brownian microscopy measurements indicated clusters with diameters of hundreds of nanometers.²¹

The results obtained by ¹³C NMR spectroscopy were quantitatively analyzed to assess the effect of sodium carbonate on formaldehyde speciation. Concentrations of formaldehyde-related species, free methanol, as well as the total formaldehyde, total methanol, and free water are summarized in Table 1.

The results show that in terms of species distribution the presence of sodium carbonate did not have a strong effect, as all three major species are present in similar proportions in all solutions. However, it can be seen that the total formaldehyde and the total methanol concentrations are about 5–10% lower (based on major species MG, MMG, and DG) in samples with sodium carbonate compared with the solution with no carbonate. This relatively small difference could be caused by some signal loss due to much slower tumbling of some fraction of molecules involved in microscopically heterogeneous solution domains.^{22,23} Although there could be some difficulties with accurate integration as peaks become significantly broader in the presence of sodium carbonate, it is unlikely that this would affect the methanol signal as well because the methanol peak does not become broader with increasing carbonate concentration.

The three major methylene glycol species present in these solutions are subject to the following chemical equilibria:



The corresponding equilibrium constants can be estimated using concentration data shown in Table 1:

$$K_1 = \frac{[\text{HO}-\text{CH}_2-\text{O}-\text{CH}_2-\text{OH}][\text{H}_2\text{O}]}{[\text{HO}-\text{CH}_2-\text{OH}]^2}$$

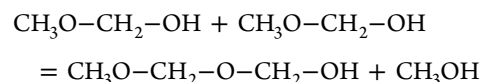
$$K_2 = \frac{[\text{CH}_3\text{O}-\text{CH}_2-\text{OH}][\text{H}_2\text{O}]}{[\text{HO}-\text{CH}_2-\text{OH}][\text{CH}_3\text{OH}]}$$

As shown in Table 2, the calculated values of equilibrium constants are very similar across all samples, even as the sodium carbonate concentration is varied.

We note that it was not possible to determine the equilibrium constant of formaldehyde hydration to form MG because no measurable amount of formaldehyde in the aldehyde form is detected in the solution. This is consistent with previous reports that this value is very high, estimated to be $\sim 2 \times 10^3$ under ambient conditions.¹³

Dimerization equilibrium constant (K_1) values obtained here can be compared with the corresponding values reported by Hahnenstein et al.⁴ for solutions prepared by depolymerization of paraformaldehyde in pure water at 293 K: $K_{\text{MG}2} = 4.92$ and 6.88 (determined by ¹H NMR and ¹³C NMR, respectively) for H₂O and $K_{\text{MG}2} = 5.96$ and 6.37 (determined by ¹H NMR and ¹³C NMR, respectively) for D₂O. These values are in good agreement with those reported here (Table 2). Note that the units for equilibrium constants reported by Hahnenstein et al. ($K_{\text{MG}2}$), expressed in terms of molar fractions are the same as those presented in this work (K_1), expressed in terms of molar concentrations.

Although we are not aware of any published values of the methoxylation equilibrium constant (K_2) in mixed solvent methanol–water solutions, previously reported equilibrium constants for MMG dimerization in purely methanolic solutions may be considered:



$$K_m = \frac{[\text{CH}_3\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{OH}][\text{CH}_3\text{OH}]}{[\text{CH}_3\text{O}-\text{CH}_2-\text{OH}]^2}$$

Hahnenstein et al. reported the value $K_m = 0.144$ and 0.127 (determined by ¹H NMR and ¹³C NMR, respectively) for methanolic solutions (no water) at 293 K, and similar values were reported by Balashov et al.⁹ using ¹³C NMR in highly methanolic solutions with some water present. Assuming that the methoxylation equilibrium constant for DG is the same as the one for MG (K_2), we can estimate the corresponding value of K_m for our system as follows: $K_m = K_1/K_2 = 5.77/45.5 = 0.127$, which is in a good agreement with previously published values.

IR spectra of formaldehyde–methanol–water solutions with and without sodium carbonate are shown in Figure 5. The 1200–800 cm^{−1} region corresponds to signals from glycols, MMGs, and methanol with assignments based on previous work.^{24–26} The main peak at 1025 cm^{−1} and the shoulder peak at 1060 cm^{−1} correspond to C–O asymmetric stretches in C–O–H, while the shoulder peak at 990 cm^{−1} corresponds to C–O asymmetric stretches in O–C–O. The peaks at 950 and 910 cm^{−1} correspond to C–O symmetric stretches in O–C–O. Finally, the peak observed at 1115 cm^{−1} corresponds to H–C–H out of plane motions in CH₃O- groups. Signals from glycols (MG and DG) therefore contribute to peaks at 910, 950, 990, 1025, and 1060 cm^{−1}, signals from MMGs contribute to (all) peaks at 910, 950, 990, 1025, 1060, and 1115 cm^{−1}, while

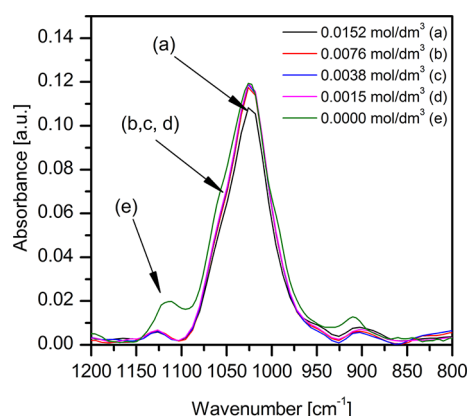


Figure 5. IR spectra at 1200–800 cm^{-1} for formaldehyde–methanol–water solutions with different concentrations of sodium carbonate as indicated.

methanol contributes to only two peaks at 1025 and 1115 cm^{-1} .

As can be seen in Figure 5, signals at 1115 (from CH_3O –groups in MMG and methanol) and 910 cm^{-1} (from C–O stretches in MG, DG, and MMG) were shifted and reduced in their intensity upon addition of sodium carbonate, while signals between 950 and 1060 cm^{-1} changed much less. Increasing the concentration of sodium carbonate did not further change the appearance of the spectrum, except for the main peak at 1025 cm^{-1} , which decreased slightly at the highest carbonate concentration. As previously discussed, the total formaldehyde and total methanol concentrations detected by liquid phase ^{13}C NMR were about 5–10% lower in samples with sodium carbonate present compared with the solution without carbonate. However, changes in the IR spectra were proportionally different for different peaks associated with formaldehyde-related species as well as for methanol. It therefore appears that the presence of sodium carbonate influences the relative contributions of various vibrations to the overall IR spectra as compared with solutions without carbonate. Considering the main peaks from 990 to 1060 cm^{-1} , corresponding to signals originating from all major species (MG, DG, MMG, and methanol) present in the solution, it can be seen that the concentration of sodium carbonate does not significantly influence species proportions, which is consistent with molecular speciation being independent of sodium carbonate concentrations, as indicated by results from ^{13}C NMR data analysis (see above).

To further investigate clustering in formaldehyde–methanol–water solutions in the presence of sodium carbonate, we used DLS to measure autocorrelation functions $g_1(\tau)$ in solutions with and without sodium carbonate. While in solutions without sodium carbonate there was no statistically significant decay behavior detected, indicating that no clusters of nanometer scale are present at detectable levels, there were well-defined exponential decays measured in solutions containing sodium carbonate (Figure 6). This indicates that there are freely diffusing clusters of colloidal dimensions present in these solutions.

As can be seen in Figure 6, as the carbonate concentration increases, the measured autocorrelation functions exhibit longer decay times, which corresponds to larger mean hydrodynamic radii ranging from 50 to 250 nm (Figure 7a). Because all solutions were filtered through 20 nm Anotop syringe filters,

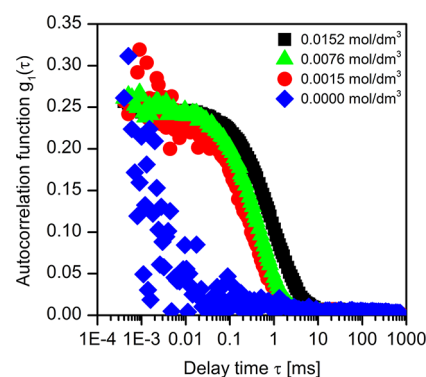


Figure 6. DLS autocorrelation function measurements in formaldehyde–methanol–water solutions with various sodium carbonate concentrations (without D_2O).

the presence of solid impurities in these solutions can be ruled out. This shows that mesoscale clusters of glycol molecules form in methanol–water solutions in the presence of sodium carbonate, with dimensions of the same order of magnitude as those formed in glycine aqueous solutions.²¹

Two types of formaldehyde–methanol–water solutions were examined, one containing pure water (H_2O) as solvent and the other containing a mixture of water and heavy water (D_2O) (7:3 v/v), which was the same as that used in NMR experiments. This was done to check the effect of D_2O addition on the observed mesoscale clusters.

Although in the presence of D_2O the mean hydrodynamic radii are ~40% lower than those in pure water, the trend with carbonate concentration was the same with or without D_2O . Also, the corresponding scattered light intensities (Figure 7b) strongly increased with increasing carbonate concentration, which would be expected for larger or more numerous clusters present in solutions with higher carbonate concentration.

We can infer from observed NMR peak broadening that the methylene glycol dimer (DG) is involved in mesoscale clusters and other formaldehyde-related species (MG and MMG) may be involved to some degree as well, while methanol appears to stay in the bulk solution. Because clusters only appear at higher pH values in the presence of sodium carbonate, it can be concluded that either pH or the presence of electrolytes is instrumental in the formation of mesoscale clusters. There are several possible mechanisms that may be at play here. It is well known that water–alcohol mixtures may undergo macroscopic liquid–liquid phase separations in the presence of electrolytes. It is therefore possible that under some conditions microphase separation may be present, where liquid-like clusters are electrostatically stabilized at colloidal scale, preventing them from growing to macroscopic scale. Furthermore, there might be electrostatic (most likely dipole) interactions among deprotonated glycols or corresponding ion pairs because at pH values observed in solutions with sodium carbonate there is a small degree of deprotonation of methylene glycols. Resulting balance of dipole and Coulombic interactions then may induce self-assembly of mesoscale clusters.

The mesoscale clusters appear to be different from polyoxometalate and other similar condensed clusters found in aqueous inorganic systems because they do not seem to involve chemical bonding between methylene glycols. Their dimensions are on the colloidal scale on the order of a hundred of nanometers, yet they are able to pass through nanofilters with pores with an order of magnitude smaller than their size.

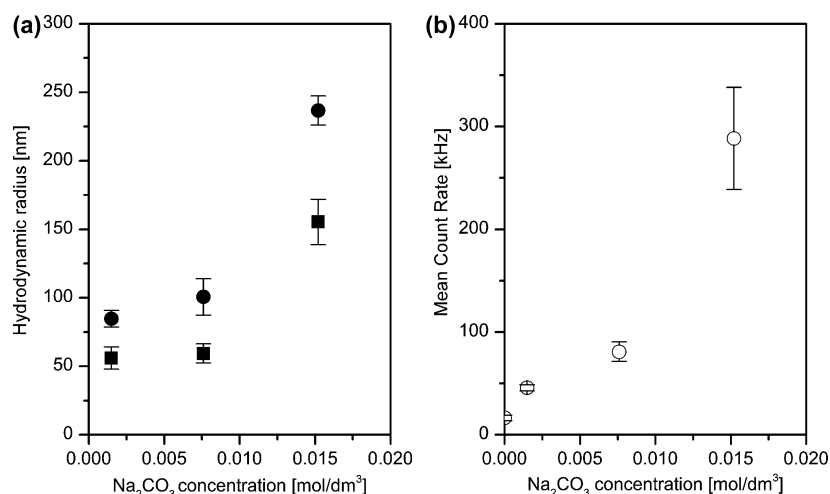


Figure 7. DLS measurements of mesoscale clusters in formaldehyde–methanol–water solutions with various sodium carbonate concentrations: (a) mean hydrodynamic radii without D₂O (circles) and with D₂O added (squares) and (b) scattered intensities for solutions without D₂O added.

This is consistent with the liquid nature of clusters, which can reversibly break and reform upon nanofiltration process, so that it can be expected that the clusters are held together by relatively weak physical interactions such as screened electrostatic interactions or hydrogen bonding. We also note that the previous work by Job and Gommès³ showed that the nature of the metal atom of the basifying agent can affect the gel formation in this system, so it can be expected that this may also have an effect on the formation of mesoscale clusters. We also suspect that the nature of the counterion, for example, HCO₃[−] versus CO₃^{2−}, may have an effect on the formation of mesoscale clusters through the role of electrolytes in micro-phase separation in formaldehyde–water–methanol solution. We note, however, that exact nature and physicochemical causes of formation of the mesoscale clusters are not fully understood and need to be the subject of further studies.

CONCLUSIONS

In this work, we have investigated for the first time the effect of a low concentration electrolyte (sodium carbonate) on the molecular speciation and mesoscale clustering in formaldehyde–water–methanol solutions at concentrations typically used in synthesis of nonporous resorcinol–formaldehyde gels. Quantitative analysis by ¹³C NMR showed that the distribution of formaldehyde-related species (glycols and methoxylated glycols) is not sensitive to carbonate concentration over a wide pH range. Further analysis of NMR spectra showed that peaks corresponding to NMR signals from formaldehyde-related species undergo significant broadening with increasing carbonate concentration, with the most pronounced effects for DG. Because the peak broadening does not seem to be related to chemical exchange, the most likely explanation for this phenomenon is a change of the spin–spin relaxation time, *T*₂. We propose that this is due to clustering of glycol molecules, which results in slower tumbling of glycol species. DLS measurements further revealed the presence of mesoscale clusters with mean hydrodynamic radii increasing from 50 to 250 nm with increasing carbonate concentration. The presence of solid impurities was ruled out by filtration of solutions with 20 nm Anotop syringe filters. In the presence of D₂O, clusters were found to be ~40% smaller, but the same trend in their size alteration with increasing carbonate concentration was found

with and without D₂O. Mesoscale clusters observed in these systems are in mutual equilibrium with the surrounding solution, forming a single microscopically heterogeneous liquid phase, similar to recently reported mesostructured liquids, such as glycine aqueous solutions as well as very well known systems, such as micellar solutions.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

MG, monoglycol (HO–CH₂–OH); MMG, methoxy monoglycol (CH₃O–CH₂–OH); DG, diglycol (HO–CH₂–O–CH₂–OH); MDG, methoxy diglycol (CH₃O–CH₂–O–CH₂–OH); TG, triglycol (HO–CH₂–O–CH₂–O–CH₂–OH); MTG, methoxy triglycol (CH₃O–CH₂–O–CH₂–O–CH₂–OH)

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