Solubility of Formaldehyde and Trioxane in Aqueous Solutions

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Formaldehyde is one of the most important C1 building blocks used in the chemical industry. It is handled in aqueous solutions, in which it is predominantly chemically bound. Solid precipitation from these solutions in the form of poly(oxymethylene)glycols imposes restrictions on many technical processes. As previously reported literature data on the solubility of formaldehyde in aqueous solutions is old, scarce, contradictory, and only very poorly documented, new measurements were carried out in the present work. Solubility data for this reactive system is reported for temperatures between 30 °C and 90 °C, corresponding to overall formaldehyde mass fractions up to about 0.81 $g \cdot g^{-1}$. The study covers also the influence of the addition of sulfuric acid and methanol. Furthermore, the solubility of trioxane, a stable cyclic trimer of formaldehyde in aqueous solutions, was studied at temperatures between 20 °C and 55 °C.

Introduction

Formaldehyde (CH_2O) is one of the most important intermediate products of the chemical industry.[1] Because of its high reactivity, formaldehyde is mainly used in aqueous solutions, which often also contain methanol. In these solutions, the concentration of monomeric formaldehyde is low, as it reacts with water and methanol, forming oligomers, namely, poly(oxymethylene)glycols ($HO(CH_2O)_nH$) in aqueous solutions and poly(oxymethylene)hemiformals ($H_3CO(CH_2O)_nH$) in methanolic solutions, respectively

$$CH_2O + H_2O \leftrightarrow HO(CH_2O)H \qquad (I)$$

$$HO(CH_2O)_{n-1}H + HO(CH_2O)H \leftrightarrow HO(CH_2O)_nH + H_2O \qquad (II)$$

$$CH_2O + CH_3OH \leftrightarrow H_3CO(CH_2O)H \qquad (III)$$

$$H_3CO(CH_2O)_{n-1}H + H_3CO(CH_2O)H \leftrightarrow H_3CO(CH_2O)_nH + CH_3OH \qquad (IV)$$

The equilibrium distribution of formaldehyde to the oligomer species depends on the overall formaldehyde concentration and temperature. Even at moderate overall formaldehyde concentrations, substantial amounts of long-chain oligomers are formed (cf. Figure 1). If a certain overall concentration of formaldehyde is exceeded, long-chain oligomers precipitate from the solutions. With increasing temperature, the solubility of the oligomers in water and methanol, respectively, increases and so does the overall formaldehyde solubility.

It is well known that the formaldehyde solubility in aqueous solutions increases strongly if a comparatively small amount of methanol is added.[1] This is in line with the fact that the average chain length of the formaldehyde oligomers in methanolic solutions is much smaller than it is in aqueous solutions.[2] This suggests the following explanation for the stabilizing effect of methanol: Formaldehyde, which was initially bound in long-chain, poorly soluble poly(oxymethylene)glycols, is transferred to short-chain and therefore better soluble poly(oxymethylene)-hemiformals. Another aspect is that methanol is a more favorable solvent for the formaldehyde oligomers than water.[3] Typical technical formaldehyde solutions contain 0.30−0.50 $g \cdot g^{-1}$ formaldehyde and 0.01−0.10 $g \cdot g^{-1}$ methanol to stabilize solution and prevent solid preciptation.

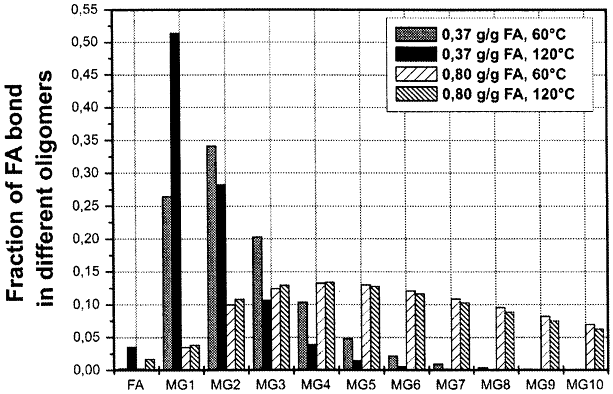

Figure 1. Distribution of formaldehyde to different species in aqueous formaldehyde solutions (prediction with the equilibrium model).[8]

Furthermore, it is shown in the present paper that the addition of electrolytes reduces the solubility of formaldehyde in water, which is the expected “salting out” effect.

Despite the extraordinary technical importance of aqueous formaldehyde solutions, the literature data on the solubility of formaldehyde in aqueous solutions is very scarce, old, and contradictory.[4−6] Furthermore, no details on the experiments, e.g., on the nontrivial preparation of the samples, are reported in the literature. Therefore, new measurements were carried out in the present work.

The solubilities measured in the present work are correlated empirically with simple polynominals. A physicochemical model for the solubility of formaldehyde can in principle be developed as an extension of the available thermodynamic equilibrium models, which aim mainly at the description of vapor−liquid equilibria. Among these

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models, the most highly developed are those of the group of Maurer,[7] the latest version from Albert in 1998.[8] The model of Maurer explicitly takes into account the chemical reactions (I−IV) and liquid-phase nonidealities. To use that model for describing the solubility, solubility constants for the individual oligomer species would have to be defined. This would, however, lead to a plethora of adjustable parameters, which could not be reasonably determined from the solubility data. In principle, the number of adjustable parameters could be reduced by using some kind of group contribution approach for the solubility constants of the oligomers. It remains an open question whether such a model would be more predictive than the simple empirical equations used here. It was not in the scope of the present work to study this in more detail.

In some industrial processes, especially polymerizations, water-free formaldehyde is needed. As pure monomeric formaldehyde is not available in the industrial scale, other routes have to be taken. One of the technically most important ways to circumvent that problem is to use trioxane, a cyclic trimer of formaldehyde.[1,4] Trioxane is a stable crystalline solid at ambient conditions. The solubility of trioxane in water is of special interest. Trioxane does not react with water unless strong acids are added (it then decomposes and releases formaldehyde). It can be regarded as a chemically inert substance for the purposes of the present study.

The literature data on the trioxane solubility in water seem to be limited to two publications.[3,9] To produce independent experimental data also, the solubility of trioxane in water was studied in the present work.

Experimental Section

The experimental setup for determining the solubility that was used in the present work consists primarily of a pressure-resistant glass vial which contains the sample and is immersed in a controlled heating bath filled with triethyleneglycol. The vial contains a magnetic stir bar and is closed by a pressure-resistant PTFE−aluminum septum through which the sample and substances such as methanol and sulfuric acid can be injected by syringes. Temperature inside the vial is measured with a calibrated PT_{100} resistance thermometer, which is inserted through the septum. Solid precipitation upon cooling is determined by visual observation.

Studies of Formaldehyde Solutions. The concentrated aqueous formaldehyde solution samples used for experiments were prepared using a thin-film evaporator, in which they are produced as bottom product. Details of the procedure are described elsewhere.[10] The feed of the evaporator was in all cases a technical aqueous formaldehyde solution (BASF, Ludwigshafen, Germany, 0.3 $g \cdot g^{-1}$ formaldehyde, 0.015 $g \cdot g^{-1}$ methanol). Depending on the chosen evaporation pressure and evaporation ratio, bottom products with formaldehyde mass fractions between 0.65 and 0.82 $g \cdot g^{-1}$ were produced. Samples with lower formaldehyde concentrations were obtained by dilution with bidistilled water. Upon partial evaporation in the thin-film apparatus, most of the methanol is removed. The methanol mass fraction in the samples that were used in the present work was always about 0.002 $g \cdot g^{-1}$. It is shown below that the presence of methanol in such low concentrations does not significantly alter the results for the formaldehyde solubility.

Before starting the experiment, a stock solution from the thin-film evaporator bottom, eventually diluted with water, was equilibrated at a temperature above 110 °C (in most cases 120 °C) for at least 5 h in a pressure-resistant vessel. Immediately before taking a sample, the stock solution was cooled in order to lower the pressure so that a pipet could be used for taking a defined amount of sample. The stock solution (10 mL) was then filled into the glass vial. This procedure was carried out in a way so that solid precipitation could not occur. The vial was closed with the septum cap. All equipment (glass vials, pipets, etc.) that comes into contact with the highly concentrated formaldehyde solution was heated to temperatures above about 110 °C.

In some experiments, sulfuric acid (0.94 $g \cdot g^{-1}$ in aqueous solution) or methanol, respectively, were added to the formaldehyde solution (mass fraction of the acid in solution either 0.015 or 0.04 $g \cdot g^{-1}$, methanol mass fraction 0.018 $g \cdot g^{-1}$). Methanol or sulfuric acid was injected directly into the vial by means of a microliter syringe through the septum. It is necessary to heat up the syringe, as an injection of cold solution immediately induces solid precipitation. Upon injection, the solution was stirred by the small magnetic stir bar in the vial.

The mass fractions of methanol and sulfuric acid in the solution were determined based on the volumetric data. The mass of the initial formaldehyde solution filled into the vial was determined by weighing. The volume of the added material (methanol or sulfuric acid) is known. The densities of injected sulfuric acid and methanol were taken from literature data.[11] Furthermore, the formaldehyde concentration and the small methanol concentration in the initial sample are known from analysis. Formaldehyde mass fractions were determined titrimetrically by the sodium sulfite method as described in ref 12. Methanol mass fractions were determined by gas chromatography (HP Gaschromatograph 5890, equipped with Chrompack Wcot Fused Silica 30 m × 0.32 mm CP Wax 52 CP DF = 0.25 μm column, split injection, and TCD detector).

After the vial was filled with the solution of the desired composition, it was re-equilibrated at the starting temperature of the experiment for at least 30 min. This temperature was above 110 °C in most cases; only when solutions with low concentrations of formaldehyde were studied was the temperature decreased. The starting temperature was always far above the expected cloud-point temperature. It was verified that the samples were initially completely clear and showed no solid precipitate. The experiments were carried out at three different cooling rates: fast (7 $K \cdot min^{-1}$), medium (2.5 $K \cdot min^{-1}$), and slow (0.067 $K \cdot min^{-1}$, corresponding to 4 $K \cdot h^{-1}$). The desired cooling rates where achieved either in the temperature-controlled heating bath by programming a temperature ramp in the case of medium and fast cooling rates or by taking the vial out of the bath and letting it cool in the air in the case of fast cooling, which turned out to give reproduceable results. The cooling rate was monitored by means of the Pt_{100} thermometer placed in the vial. The sample was continuously observed visually. The cloud-point temperature (solid precipitation) was read.

In solutions with formaldehyde mass fraction above about 0.6 $g \cdot g^{-1}$, the cloud point is well defined. In solutions with lower formaldehyde mass fractions, clouding happens slowly and is more difficult to observe. If the temperature is increased again shortly after the clouding is observed, a clear solution is obtained again. If, however, the temperature is reduced further, the whole sample may become solid, and a subsequent increase of the temperature will not lead again to a clear solution. Extrapolation studies at different cooling rates showed that the cloud-point temperature observed in the experiments at the slowest cooling

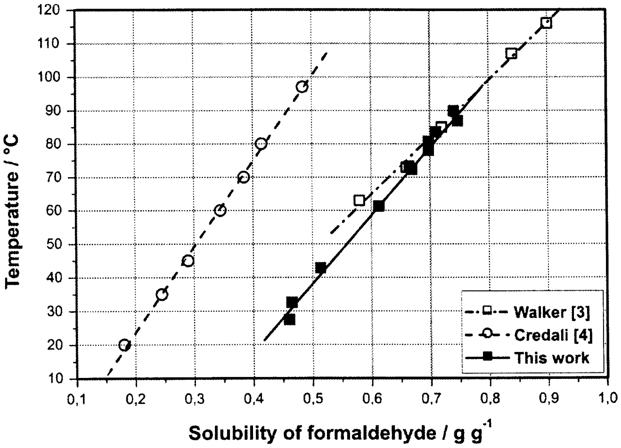

Figure 2. Solubility of formaldehyde in aqueous solutions. Experimental data from the present work and literature.

rate can be considered as the solubility temperature.

It should be mentioned here that, in some cases, when initially clear and equilibrated samples of formaldehyde solutions were stored at temperatures above the solubility temperature, determined as described above, after several days or weeks, respectively, solid precipitation occurred. This effect was only poorly reproducible and could therefore not be studied in detail. If that effect is not an artifact, its time scale must be distinctly longer than that usually considered in solubility measurements. The effect might, however, be important for long-term storage of formaldehyde solutions.

The overall accuracy of the data is mainly determined by the difficulties in preparing and handling the samples and the visual observation of the cloud point. The repeatability of the measurement of the cloud point is typically about 1−2 K. The accuracy of the temperature measurement itself is much better (about 0.1 K); the accuracies of the mass fraction measurement is about 2% for formaldehyde (relative error) and 0.01 $g\cdot g^{-1}$ for methanol and sulfuric acid (absolute errors in the mass fraction).

Studies of Trioxane Solutions. Water−trioxane solutions were prepared by disolving a known amount of trioxane (Fluka Chemika, purity > 99%) in bidistilled water. The experimental procedure for detecting the trioxane solubility was similar to that used for the studies of the formaldehyde solutions. The cloud point of the water−trioxane samples is well defined and reproduceable.

The data reported here were obtained at cooling rates of 7 $K\cdot min^{-1}$ and 0.067 $K\cdot min^{-1}$. Both data sets show no systematic deviation and are therefore considered as solubility data. The overall error in the determination of the solubility temperature is estimated to be 1 K. The error in the determination of the mass fraction is negligible.

Results and Discussion

Formaldehyde Solutions. The results of the measurements of the solubility of formaldehyde in aqueous solutions (without addition of methanol or sulfuric acid, obtained at slow cooling rate) are shown in Figure 2 together with data from the literature. Numerical results of the experiments of the present work are presented in Table 1. As can be seen from Figure 2, the agreement between the data from the present work and Walker's data,[4] which are 50 years old, is acceptable, whereas extreme deviations are observed from Credali's data.[5] As neither Credali nor Walker specify their experimental conditions, a more detailed discussion of these findings is not possible. It is obvious that the data from the present work and Walker's data should be preferred.

Table 1. Solubility of Formaldehyde in Aqueous Solutions

condition	formaldehyde mass fraction/$g\cdot g^{-1}$	T/°C
0.0 $g\cdot g^{-1}$ H_2SO_4 0.002 $g\cdot g^{-1}$ CH_3OH	0.461 0	27.46
	0.464 8	32.60
	0.513 4	42.83
	0.613 2	61.32
	0.664 7	73.38
	0.669 1	72.31
	0.679 9	66.98
	0.697 5	78.05
	0.697 5	80.72
	0.710 0	83.59
	0.740 7	89.88
	0.745 7	86.86
0.015 $g\cdot g^{-1}$ H_2SO_4 0.002 $g\cdot g^{-1}$ CH_3OH	0.513 4	45.37
	0.585 4	77.61
	0.649 0	83.69
	0.697 5	90.12
	0.710 0	100.00
	0.740 8	95.48
	0.745 7	102.62
0.015 $g\cdot g^{-1}$ H_2SO_4 0.018 $g\cdot g^{-1}$ CH_3OH	0.451 2	22.21
	0.483 5	39.30
	0.604 7	61.18
	0.628 4	64.50
	0.689 5	78.60
	0.695 8	82.07
	0.740 8	89.56
	0.745 7	101.61
0.0 $g\cdot g^{-1}$ H_2SO_4 0.018 $g\cdot g^{-1}$ CH_3OH	0.464 8	22.04
	0.496 7	39.02
	0.605 7	52.38
	0.693 5	69.00
	0.733 4	80.38
	0.764 7	88.25

The data from the present work can be correlated by

$$(T/°\mathrm{C}) = 204.30(x_{\mathrm{FA}}/\mathrm{g}\cdot\mathrm{g}^{-1}) - 64.07 \quad \text{for} \quad x_{\mathrm{FA}}/\mathrm{g}\cdot\mathrm{g}^{-1} > 0.45 \quad (1)$$

The experimental data from the present work scatter around that correlation with a mean deviation of about 2 K, which is acceptable regarding the complicated handling of the solutions.

Figure 3 shows the influence of the cooling rate on the cloud-point temperature. An increase of the cooling rate from 0.067 $K\cdot min^{-1}$ to about 7 $K\cdot min^{-1}$ leads to a decrease of the observed cloud-point temperature of about 8 K.

The results of the experimental investigations of formaldehyde solutions with methanol and sulfuric acid are presented in Figure 4. All experiments shown in that figure were carried out at a slow cooling rate and can be considered as solubility data. The addition of sulfuric acid lowers the solubility of formaldehyde. If 0.015 $g\cdot g^{-1}$ of sulfuric acid is added to an aqueous formaldehyde solution at the solubility limit, the temperature must be increased by about 12 K to avoid solid precipitation. That salting-out effect of sulfuric acid can be explained by the well-known fact that the ions bind water in their solvation shells. The addition of sulfuric acid also leads to increased reaction rates of reactions I−IV.[13] That acceleration of reaction kinetics has probably no influence on the observed shift of the cloud-point temperature, as the cooling rate was very slow and the temperatures were fairly high so that the reaction can be considered to be in chemical equilibrium during the entire cooling process. Furthermore, the chemi-

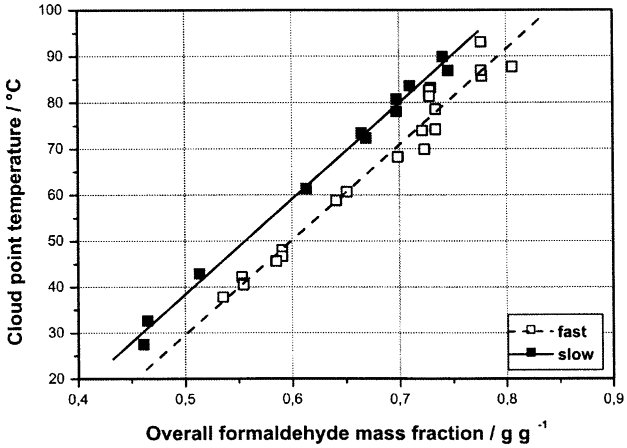

Figure 3. Influence of the cooling rate (slow, 0.067 K·min^{-1}; fast, 7.0 K·min^{-1}) on the observed cloud-point temperature in aqueous formaldehyde solutions. The experiments at the slow cooling rate can be considered as solubility data.

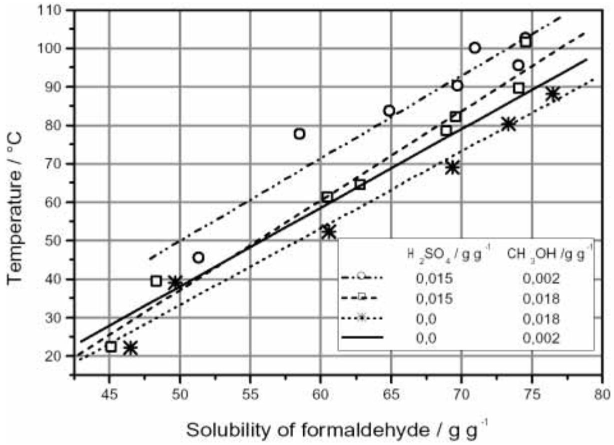

Figure 4. Influence of the addition of methanol and sulfuric acid on the solubility of formaldehyde in aqueous solutions.

cal equilibria in aqueous formaldehyde solutions are only weakly temperature dependent.[7]

As expected, the addition of methanol increases the solubility of formaldehyde. The addition of about 0.015 g·g^{-1} of methanol has a comparable effect on the solubility of formaldehyde as an increase of the temperature of about 5 K (cf. Figure 4). The reasons for this effect have already been discussed in the Introduction. Figure 4 also contains results from a series of experiments, in which both sulfuric acid and methanol were added. The adverse influence on the formaldehyde solubility of both agents at least partially compensate each other, and the observations in that series of measurements can be interpreted as a superposition of both individual effects (cf. Figure 4).

Assuming a linear dependence of the formaldehyde solubility on the methanol concentration allows us to give an estimate of the influence of the small methanol concentration in the samples from the thin-film evaporator on the solubility data. As the methanol concentration in the sample from the thin-film evaporator was about a factor of 6.5 below the methanol concentration in the samples studied in the experiments shown in Figure 4, it can be estimated that the shift of the solubility temperature due to the presence of these small amounts of methanol is at best of the order of 0.5 K and hence within the scattering of the data.

Trioxane Solutions. The results of the measurements of the solubility of trioxane in water are shown in Figure 5, together with data from literature (Sagu et al.[3] and Brandani[9]). Numerical results from the experiments of the present work are presented in Table 2. The solubility data shows a s-shaped dependence on the trioxane mass fraction. The different cooling rates used here have no discernible effect on the determined solubility temperature. For this reason, all results, independent from cooling rate, were combined in Figure 5.

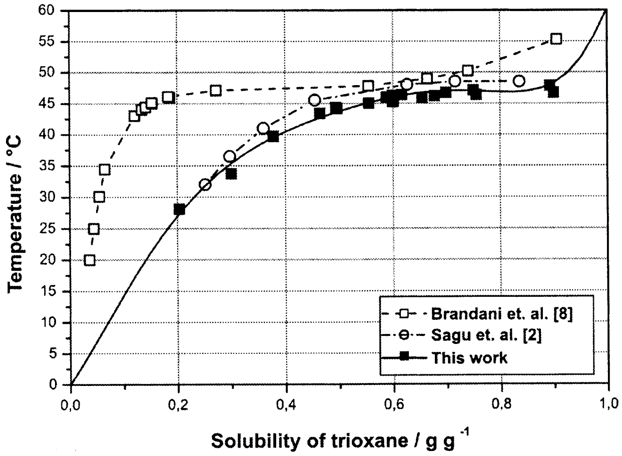

Figure 5. Solubility of trioxane in water. Experimental data from the present work and literature.

Table 2. Solubility of Trioxane in Aqueous Solutions

trioxane mass fraction/g·g^{-1}	cloud-point T/°C
0.2037	28.13
0.3000	33.72
0.3781	39.73
0.4643	43.39
0.4941	44.35
0.4960	44.20
0.5551	45.00
0.5880	45.96
0.5992	46.25
0.5999	45.24
0.6011	45.37
0.6159	46.38
0.6540	45.90
0.6776	46.19
0.6990	46.74
0.7495	47.14
0.7551	46.38
0.8928	47.86
0.8994	46.73

The data from the present work and Sagu's data[3] show fair agreement, whereas large deviations from Brandani's data[9] occur. While the experimental setup in Sagu's work was comparable to the present work, Brandani determined solubility from decanting a saturated solution of water and trioxane and analyzing it with gas chromatography. A similar procedure as Brandani's was also used in the present work to test properties for two samples. The results were in full agreement with the data reported here.

The data of the trioxane solubility in water from the present work can be correlated by

$$(T/°\mathrm{C}) = 1865.6(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}})^6 - 5146.7(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}})^5 + 5378.7(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}})^4 - 2533.2(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}})^3 + 369.7(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}})^2 + 126.93\,(x_{\mathrm{TRI}}/\mathrm{g\cdot g^{-1}}) \quad (2)$$

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Nomenclature

x_i = mass fraction of component i
FA = formaldehyde
MG(n) = poly(oxymethylene)glycols with n CH_2O segments
T = temperature
TRI = trioxane

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