Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

Appendix A

Correlations for the density and viscosity of aqueous formaldehyde solutions

Abstract

Empirical correlations are presented for the density and viscosity of aqueous formaldehyde solutions as a function of temperature ($T$) and overall weight percentage of formaldehyde ($W_f$). Experimental density data from the literature, at $T = 288-338$ K and with $W_f = 1.6-50$ wt %, are described with an average absolute residual (AAR) of 0.14%. Experimental viscosity data, both new and from the literature, at $T = 288-333$ K and with $W_f = 1.6-50$ wt %, are described with an AAR of 1.8%. The residuals of the correlations are free of trending effects as a function of $T$ and $W_f$. It is shown that both properties can be described using liquid mixture correlation methods from the literature with almost the same accuracy relative to the empirical correlations.

Introduction

Formaldehyde is an important industrial base chemical. One of the key steps in its production is the absorption of gaseous formaldehyde in water, usually in a packed absorber. The performance of the absorbers depends on the process operation variables, such as the temperature, the pressure, and the flow rates, and on the hydrodynamic properties of the packing, such as the mass-transfer coefficients, the specific interfacial area, and the liquid phase hold-up in the packing. Therefore, in modelling, design, and optimisation calculations of the formaldehyde absorbers, the hydrodynamic properties have to be evaluated. In the literature these parameters are usually correlated to, among other things, the liquid-phase physical properties, especially the density and viscosity. Also, in the specification sheets of packing manufacturers, the performance of the packing types is often given as a function of these liquid-phase properties, along with various flow-rate parameters.

Two literature sources were found giving correlations for the density of aqueous formaldehyde solutions, $\rho_m$. Walker (1964) gives a correlation for $\rho_m$ as a function of the strength of the solution, $W_f$, which is valid at 291 K only,

$$ (\rho_m)_{291\text{K}} = 1.00 \times 10^3 + 3W_F \quad (T = 291\text{K}), \quad (1) $$

and the temperature coefficients in the range of $T = 288-303$ K for $W_f = 15$ and 45 wt %, from which, using eq (1), the following correlations can be obtained:

$$ (\rho_m)_{15\text{wt\%}} = 1045 + 0.2(291 - T) \quad (W_f = 15\text{ wt\%}, T = 288-303\text{K}), \quad (2) $$

$$ (\rho_m)_{45\text{wt\%}} = 1135 + 0.4(291 - T) \quad (W_f = 45\text{ wt\%}, T = 288-303\text{K}). \quad (3) $$

The *Kirk-Othmer Encyclopedia of Chemical Technology* (1994) presents a correlation for $\rho_m$ which reads (slightly modified to yield consistent units)
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

\[ \rho_m = [11.19 + 3(W_F - 45)][1.0 + 0.55 \times 10^{-3}(328 - T)] \text{.} \]  
(4)

No information is given on the accuracy of eq (4), nor on the temperature and concentration range for which it is valid. The same source also presents a correlation of the viscosity of aqueous formaldehyde solutions, \( \eta_m \), which slightly modified reads

\[ \eta_m = 10^{-3}[1.28 + 0.039W_F - 0.024(T - 273.15)] \text{.} \]  
(5)

Equation (5) is valid for rather concentrated solutions, \( W_F = 30\text{-}50 \text{ wt } \% \), and for \( T = 298\text{-}313 \text{ K} \). No information is given on the accuracy of eq (5).

In this contribution the results of a study to correlate the available literature data on \( \rho_m \) and \( \eta_m \) as a function of \( T \) and \( W_F \) are reported. Also, the results of a series of viscosity measurements of aqueous formaldehyde solutions are reported.

**Density**

Three literature sources were found reporting data on \( \rho_m \); see Table 1. Lileev et al. (1982) specified the strength of the solutions in terms of the overall formaldehyde molar fraction, \( \bar{x}_F \), from which we calculated \( W_F \), because these units were used by the other authors mentioned in Table 1:

\[ W_F = \frac{\bar{x}_FM_F}{\bar{x}_FM_F + (1 - \bar{x}_F)M_W} \times 100\% \text{.} \]  
(6)

The experimental results show that \( \rho_m \) varies with \( T \) and \( W_F \) and that always \( \rho_m > \rho_W \) (for \( W_F > 0 \)). Fig. 1 shows the density difference \( (\rho_m - \rho_W) \) as a function of \( W_F \), with \( \rho_W \) from Perry et al. (1984). It shows that a considerable fraction of the observed variation of \( \rho_m \) can be accounted for by introducing a linear dependency of \( (\rho_m - \rho_W) \) on \( W_F \). Least-squares regression of the data accordingly, followed by an analysis of the residuals, \( \Delta_i \), defined as

\[ \Delta_i = \left( \frac{(\rho_m)_{\text{calc}} - (\rho_m)_{\text{exp}}}{(\rho_m)_{\text{exp}}} \right)_i \times 100\% \text{.} \]  
(7)

showed that the residuals have a clear trend as a function of \( T \), indicating an inadequacy in the relation which makes extrapolation unreliable outside the applied experimental conditions. The residuals tend to increase monotonically with increasing \( T \), justifying the introduction of an additional temperature-dependent parameter. Using multiple regression the following equation was thus obtained:

\[ \rho_m = \rho_W + (5.0950 - 6.8166 \times 10^{-3}T)W_F \text{.} \]  
(8)
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

Table 1. Literature data on the density of aqueous formaldehyde solutions.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>T (K)</th>
<th>W_f (wt %)</th>
<th>ρ_m (kg m⁻³)</th>
<th>data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>291-338</td>
<td>2-50</td>
<td>1005.4-1570.0</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>288, 298</td>
<td>6-43</td>
<td>1018.4-1135.4</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>288, 298, 308</td>
<td>1.6-17</td>
<td>997.4-1045.4</td>
<td>15</td>
</tr>
<tr>
<td>all</td>
<td>288-338</td>
<td>1.6-50</td>
<td>997.4-1570.0</td>
<td>58</td>
</tr>
</tbody>
</table>

Fig. 1. Density difference between aqueous formaldehyde solutions and water, both at the same temperature. ρ_m: from the literature sources indicated. ρ_W: Perry et al. (1984).

When eq (8) was applied to a 15 wt % solution, at 288 ≤ T ≤ 303 K, the difference with eq (2) (Walker, 1964) was always less than 0.1%. Similarly, with a 45 wt % solution, at the same temperatures, the difference between eqs (8) and (3) (Walker, 1964) was no more than 0.3%.

For eq (8) an average absolute residual (AAR) of 0.14% was found, with a maximum absolute residual (MAX) of 0.69%. The AAR is calculated from

$$ AAR = \frac{1}{n} \sum_{i=1}^{n} |\Delta_i| $$  \hspace{1cm} (9)

More importantly, however, the residuals obtained with eq (8) do not show any systematic variation with T or W_f, see Figs 2 and 3. Therefore, eq (8) is a reliable empirical equation for ρ_m. With eq (4) (Kirk-Othmer Encyclopedia of Chemical Technology, 1994) an AAR of 0.42% (MAX of 1.8%) was observed, which is 3 times as high as the value of eq (8).
Many literature methods for the calculation of liquid mixture densities use the critical properties and acentric factors, i.e., vapour pressure vs. temperature correlations, of the individual components (e.g., Reid et al., 1988) and are therefore not suitable here because the required properties of the higher poly(oxymethylene) glycols (POMs) are unknown. Although Amagat's law originally holds strictly only for mixtures of ideal gases, it is also recommended for the calculation of liquid densities of mixtures of similar components (Perry et al., 1984),

$$V_m = \sum_i^n V_i.$$  

(10)
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

To apply eq (10), the composition of the liquid has to be considered. In aqueous solutions, formaldehyde is hydrated to methylene glycol and a series of POMs:

\[ \text{CH}_2\text{O} + \text{H}_2\text{O} \iff \text{CH}_2(\text{OH})_2, \]
\[ \text{HO(\text{CH}_2\text{O})_i + \text{CH}_2(\text{OH})_2 \iff HO(\text{CH}_2\text{O})_{i+1} + \text{H}_2\text{O} \quad (i = 1, \infty).} \]

Methylene glycol and the POMs only exist in formaldehyde solutions. They cannot be isolated in a pure form, and their pure-component properties cannot be measured directly.

The equilibrium of eq (11) is far to the right and the concentration of free formaldehyde in aqueous solutions is negligible compared to those of methylene glycol and the higher POMs. Then, for the formaldehyde-water system, Amagat’s law can be written as

\[ V_m = V_w x_w + \sum_{i=1}^{\infty} (V_w + i V_F) x_{WF_i}, \]  

where it is assumed that the molar volumes of the POMs can be written as the sum of the volumes of the constituent groups. The subscript WF\(i\) denotes HO(\text{CH}_2\text{O})_i\text{H}, i.e., the component consisting stoichiometrically of water and \(i\) formaldehyde units.

With the molar balance

\[ x_w + \sum_{i=1}^{\infty} x_{WF_i} = 1, \]

the overall formaldehyde balance

\[ \bar{x}_F = \frac{\sum_{i=1}^{\infty} i x_{WF_i}}{x_w + \sum_{i=1}^{\infty} (i + 1) x_{WF_i}}, \]

and the substitution \( V = M \rho \), eq (13) can be rewritten as

\[ \frac{M_m}{\rho_m} = \frac{M_w}{\rho_w} + \frac{\bar{x}_F V_F}{1 - \bar{x}_F} V. \]

Because every molecule in the solution is either a free water molecule or a water molecule chemically bonded to one or more formaldehyde units, the true total concentration in the solution is equal to the overall water concentration. Therefore, the true mean molar weight of the solution, \( M_{m} \), can be obtained as

\[ M_{m} = \frac{M_w}{1 - (V_F / 100)}, \]
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

and the model equation for the density of aqueous formaldehyde solutions, from inserting eqs (6) and (17) in eq (16) and rewriting, becomes

$$\rho_m = \frac{100 \rho_M M_F}{(100 - W_F) M_F + \rho_M W_F V_F}$$  \hspace{1cm} (18)

The only parameter in eq (18) to be determined from the experimental data is the molar volume of the CH₂O groups in the POM molecules, $V_F$. By taking $V_F$ constant, an AAR of 0.45% was obtained (MAX of 1.7%). Not surprisingly, however, taking $V_F$ constant resulted in a clear trend of the residuals of eq (18) as a function of $T$, varying in the expected direction, i.e., from negative values at the lower temperatures to positive values at the higher temperatures.

Because of the clear trend of the residuals, a second parameter to account for the influence of $T$ on $V_F$ seems justified. Least-squares analysis of the experimental data according to eq (18) resulted in the following optimum parameters for $V_F$:

$$V_F = 12.709 \times 10^{-3} + 30.59 \times 10^{-6} T$$  \hspace{1cm} (19)

Figs 4 and 5 illustrate the relative residuals of $\rho_m$ calculated with eqs (18) and (19) as a function of $W_F$ and $T$. No trend in the residuals was found. Here, an AAR of 0.22% was found (MAX of 0.69%).

At first glance, eqs (8) and (18) might seem paradoxical: eq (8) correlates $\rho_m$ linearly with $W_F$, while eq (18) correlates $1/\rho_m$ similarly. This is not a true inconsistency because the coefficient of $W_F$ is positive in eq (8), resulting in an increase of $\rho_m$ with an increase of $W_F$, whereas the overall coefficient of $W_F$ in the denominator of eq (18) is negative, giving the same direction of variation of $\rho_m$ with $W_F$.

![Fig. 4](image-url)  
Fig. 4. Relative residuals of the density correlation obtained from Anmagat's law (eq 18) as a function of the temperature. Symbols: see Fig. 1.
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

Fig. 5. Relative residuals of the density correlation obtained from Anmagat's law (eq 18) as a function of $W_f$. Symbols: see Fig. 1.

Viscosity

Table 2 summarizes literature data on the viscosity of aqueous formaldehyde solutions. Because this data set is rather limited, we performed additional viscosity measurements with a Schott automated viscosity meter (described in more detail by Soliman & Marschall, 1990). The solutions were prepared by dissolving a desired amount of paraformaldehyde (Janssen Chimica) in distilled water. By keeping high efflux times (120-360 s), the error due to kinetic energy was assumed negligible. Although the vapour pressure of pure formaldehyde at the highest temperature of the measurements, $325 \, \text{K}$, is more than 1.1 MPa (Reid et al., 1988), its concentration is so low because of the reactions (11) and (12) that the formaldehyde vapour pressure over a 33 wt % solution is only approximately 1 kPa (Maurer, 1986). Thus, the influence of possible evaporation of formaldehyde on the measurements is neglected. The viscometer was calibrated at each temperature using pure water. The absolute viscosity was determined from the measured kinematic viscosity using the density obtained from eq (8). The results are shown in Table 3, where each data point is the mean of three measurements whose flow times were within 0.15 s. The total uncertainty of the viscosity data was estimated to be $\pm 1.5 \%$.

Table 2. Literature data on the viscosity of aqueous formaldehyde solutions.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$W_f$ (wt %)</th>
<th>$\eta_m \times 10^3$ (Pa s)</th>
<th>data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298, 333</td>
<td>5-50</td>
<td>0.54-1.87</td>
</tr>
<tr>
<td>4</td>
<td>288, 298, 308</td>
<td>1.6-17</td>
<td>0.7487-1.6086</td>
</tr>
<tr>
<td>all data</td>
<td>288-333</td>
<td>1.6-50</td>
<td>0.54-1.87</td>
</tr>
</tbody>
</table>
Table 3. New experimental data on the viscosity of aqueous formaldehyde solutions.

<table>
<thead>
<tr>
<th>$W_F$ (wt %)</th>
<th>$T = 297.85$ K</th>
<th>$T = 307.15$ K</th>
<th>$T = 318.05$ K</th>
<th>$T = 325.25$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.0295</td>
<td>0.8417</td>
<td>0.6830</td>
<td>0.6011</td>
</tr>
<tr>
<td>15</td>
<td>1.2853</td>
<td>1.0537</td>
<td>0.8470</td>
<td>0.7465</td>
</tr>
<tr>
<td>25</td>
<td>1.6377</td>
<td>1.3365</td>
<td>1.0619</td>
<td>0.9279</td>
</tr>
<tr>
<td>33</td>
<td>2.0456</td>
<td>1.6483</td>
<td>1.3129</td>
<td>1.1277</td>
</tr>
</tbody>
</table>

Over a wide temperature range, the logarithm of the kinematic viscosity, $\eta / \rho$, uses to correlate linearly with $1/T$ for pure liquids (Reid et al., 1988). This appears also to hold for formaldehyde solutions for a constant $W_F$. The influence of the composition could be accounted for by correlating $\ln(\eta_m / \rho \_M_m)$ linearly both to $1/T$ and $W_F$. Finally, from an analysis of the residuals it was found that an additional term, linearly with $T$, was needed to obtain a correlation free of trending effects of the residuals. The empirical correlation developed this way is

$$\ln \left( \frac{\eta_m}{\rho \_M_m} \right) = -47.90 + \frac{5644}{T} + 9.36 \times 10^{-3} W_F + 0.0404 T,$$

(20)

with an AAR of 1.8% (MAX of 7.5%) for $288 \leq T \leq 333$ K. $\rho_m$ and $M_m$ are obtained from eqs (8) and (17), respectively. Equation (20) is illustrated in Fig. 6. The residuals of eq (20) did not show any clear trend as a function of $W_F$ or $T$, see Figs 7 and 8.

Fig. 6. $\eta_m/\rho \_M_m$ as a function of $W_F$ for various $T$. Symbols: $\eta_m$ from the sources indicated, $\rho_m$ and $M_m$ from eqs (8) and 17, respectively. Lines: $\eta_m/\rho \_M_m$ calculated with the empirical viscosity correlation (20).
Fig. 7. Relative residuals of the empirical viscosity correlation (20) as a function of $W_F$.
Symbols: see Fig. 6.

Fig. 8. Relative residuals of the empirical viscosity correlation (20) as a function of $T$.
Symbols: see Fig. 6.

In addition to eq (20), we also tested an Antoine-type of temperature dependency, augmented with a linear term in $W_F$, i.e., $\ln(\eta/\rho_{\infty}M_m) = p_1 + p_2/(T + p_3) + p_4 W_F$. After optimization of the parameters using nonlinear regression, the same AAR (1.8%) was observed; however, MAX was somewhat larger (8.6%) as compared to eq (20).
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

The methods found in the literature for obtaining the viscosity of liquid mixtures are often based on the mole fraction average of the logarithms of the pure-component viscosities, extended with various types of correction factors (Perry et al., 1984; Reid et al., 1988). Applying mole fraction averaging to the formaldehyde-water system gives

$$\ln \eta_m = x_w \ln \eta_W + \sum_{i=1}^{\infty} x_{WF_i} \ln \eta_{WF_i}.$$  (21)

In the literature it is shown that for various homologous series the logarithm of the pure-component viscosities varies linearly with the molecular size (e.g. Chase, 1984; Allan & Teja, 1991; Nhaesi & Asfour, 1998). This concept cannot be tested directly for methylene glycol and the POMs, because they cannot be obtained in pure form.

However, experimental viscosity data are available for the closely related series of ethylene glycol and the poly(ethylene glycols) HO(CH₂CH₂O)ᵢH or PEGᵢ. Here, we will use these data just to illustrate the concept before returning attention to the aqueous formaldehyde solutions. We found that for $294 \leq T \leq 333$ K the viscosities of PEGᵢ can be described by

$$\ln \eta_{PEGᵢ} = a + ib,$$  (22)

with $a = -15.60 + 3406 / T$ and $b = -0.1925 + 132.8 / T$. Fig. 9 shows experimental data of the viscosities of PEGᵢ (i=1..6) and the straight lines calculated with eq 22. Although the viscosity of the monomer, ethylene glycol, deviates somewhat, the overall agreement is satisfactory considering the simplicity of the correlation.

![Fig. 9. Viscosity of poly(ethylene glycol) as a function of the molecular size i at various T. Symbols: experimental data from the sources indicated. Lines: calculated with eq (22).](image-url)
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

Assuming this concept also applies to the series of methylene glycol and the higher POMs gives

\[
\ln \eta_{WF} = A + iB. \tag{23}
\]

With eqs (14), (15) and (23), eq (21) can be rewritten as

\[
\ln \eta_m = x_W \ln \eta_W + (1 - x_W)A + \frac{x_F}{1 - \bar{x}_F}B. \tag{24}
\]

Least-squares regression of the experimental data to eq (24) resulted in the following parameter values:

\[
A = 17.97 - 7174/T, \quad B = -14.72 + 5048/T. \tag{25}
\]

The true molar fraction of water, \(x_{W_t}\), in the solutions was calculated by solving the equilibrium equations for the reactions (12)

\[
\frac{x_{WF2}x_W}{x_{WF1}} = K_2, \tag{26}
\]

\[
\frac{x_{WF3}x_W}{x_{WF4}x_{WF1}} = K_3 \quad (i \geq 3), \tag{27}
\]

simultaneously with the balances (14) and (15), where \(\bar{x}_F\) was obtained from eq 6. The equilibrium constants \(K_2\) and \(K_3\) for the formaldehyde-water system were taken from Hahnenstein et al. (1994)

![Fig. 10. Viscosity of aqueous formaldehyde solutions. Symbols: experimental data, see Fig. 6. Lines: calculated with eq (24).](image-url)
The accuracy of eq (24) is comparable to that of eq (20) (AAR of 2.0% and MAX of 7.6%). The correlation is illustrated in Fig. 10. The residuals do not show any trend as a function of $T$ or $W_f$ as shown in Figs (11) and (12).

When applied to all of the data, the errors of eq (5) (Walker, 1964) for the viscosity of aqueous formaldehyde solutions were large (AAR of 15.6% and MAX of 93%). When only the data within the ranges of $W_f = 30-50$ wt % and $T = 298-313$ K were considered, an AAR of 3.5% (MAX of 6.2%) was obtained, thereby demonstrating the more limited applicability of eq (5).

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![Fig. 11. Relative residuals of the viscosity correlation (24) as a function of $W_f$. Symbols: see Fig. 6.](image1)

![Fig. 12. Relative residuals of the viscosity correlation (24) as a function of $T$. Symbols: see Fig. 6.](image2)
Appendix A: Correlations for the density and viscosity of aqueous formaldehyde solutions.

Conclusions

The density and viscosity of aqueous formaldehyde solutions can be accurately and reliably obtained as a function of the temperature and the strength of the solution with the simple empirical correlations obtained here. The empirical density correlation (eq 8) employs two adjustable parameters that were optimised using three literature sources of density data. The empirical viscosity correlation (eq 20) has four coefficients that were optimised using two literature data sources together with a series of new additional measurements.

The residuals of the correlations presented are free of trending effects as a function of both the temperature and the weight percentage of formaldehyde. Therefore, we conclude that the correlations can be used reliably in engineering calculations with a small extrapolation to cover the entire range of conditions prevailing in formaldehyde absorbers, i.e., $280 \leq T \leq 340\,\text{K}$ and $0 \leq W_F \leq 60\,\text{wt\%}$.

A mixture density correlation method from the literature, where the molar volume of the mixture is obtained as the molar fraction average of the pure-component molar volumes, appeared to represent the data with almost the same accuracy. In this case two coefficients were fitted to the data, to correlate the molar volume of the CH$_2$O groups linearly to the temperature.

Similarly, a literature method for liquid mixture viscosities, where the logarithm of the pure-component viscosities are molar fraction averaged, resulted in almost the same accuracy relative to the empirical correlation. In this case, it was assumed that the logarithm of the viscosities of the homologous series of methylene glycol and the higher POMs varies linearly with the molecular size of the components. This way, the molar fraction average method contains two temperature-dependent parameters, i.e., four adjustable coefficients.

At first glance it seems surprising that the empirical relations for the density (eq 8) and viscosity (eq 20) both result in somewhat lower AAR values as compared to the relations that were arrived at starting from methods found in the literature (eqs 18, 19 and 24, respectively), even though in both cases the same number of coefficients were adjusted to the experimental data. This may reflect, however, the difficulties still encountered at present in the development of theory applicable to estimating liquid mixture properties.
Appendix B

Equilibrium molar fractions in aqueous methanolic formaldehyde solutions

In aqueous mixtures of formaldehyde and methanol, the equilibrium composition is determined by a series of reactions:

\[
\begin{align*}
\text{CH}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_2(\text{OH})_2, \\
2\text{CH}_2(\text{OH})_2 & \rightleftharpoons \text{HO(} \text{CH}_2\text{O})_2\text{H} + \text{H}_2\text{O}, \\
\text{HO(} \text{CH}_2\text{O})_{i-1}\text{H} + \text{CH}_2(\text{OH})_2 & \rightleftharpoons \text{HO(} \text{CH}_2\text{O})_i\text{H} + \text{H}_2\text{O} \quad (i = 3 \cdots \infty), \\
\text{CH}_2\text{O} + \text{CH}_3\text{OH} & \rightleftharpoons \text{CH}_3\text{OCH}_2\text{OH}, \\
\text{CH}_3\text{O(} \text{CH}_2\text{O})_{i-1}\text{H} + \text{CH}_3\text{OCH}_2\text{OH} & \rightleftharpoons \text{CH}_3\text{O(} \text{CH}_2\text{O})_i\text{H} + \text{CH}_3\text{OH} \quad (i = 2 \cdots \infty).
\end{align*}
\]

The equilibrium conditions, in terms of molar fractions, for the reactions read:

\[
\begin{align*}
K_1 &= \frac{x_{WF_i}}{x_F \cdot x_W}, \\
K_2 &= \frac{x_{WF_i} \cdot x_W}{x_{WF_i}}, \\
K_3 &= \frac{x_{WF_i} \cdot x_W}{x_{WF_i} \cdot x_{WF_i}} \quad (i = 3 \cdots \infty), \\
K_{M1} &= \frac{x_{MF_i}}{x_F \cdot x_M}, \\
K_{M2} &= \frac{x_{MF_i} \cdot x_M}{x_{MF_i} \cdot x_{MF_i}} \quad (i = 2 \cdots \infty).
\end{align*}
\]

In addition, three overall balances combine the overall molar fractions, \( \tilde{x}_F, \tilde{x}_W \) and \( \tilde{x}_M \), with the true molar fractions in the mixture:

\[
\tilde{x}_F = \frac{x_F + \sum_{i=1}^{\infty} i x_{WF_i} + \sum_{i=1}^{\infty} i x_{MF_i}}{1 + \sum_{i=1}^{\infty} i x_{WF_i} + \sum_{i=1}^{\infty} i x_{MF_i}},
\]

\[117\]
Appendix B: Equilibrium molar fractions in aqueous methanolic formaldehyde solutions

\[ \sum \sum \sum_{i=1}^{\infty} i \omega_{i} = \sum \sum_{i=1}^{\infty} i \omega_{i} = \sum \sum_{i=1}^{\infty} i \omega_{i} \]

The set of eqs (6)-(13), in principle, provides enough information to calculate all molar fractions. However, we have an infinite number of eqs (8) and (10), and the summations in (11)-(13) have no upper limit. These problems can be overcome by using some simple properties from the theory of power series. Thus, by substitution of the molar fractions of the reaction products obtained from (7)-(10), the summations in (11)-(13) can be written as

\[ \sum_{i=1}^{\infty} \omega_{i} = \sum_{i=1}^{\infty} \omega_{i} = \sum_{i=1}^{\infty} \omega_{i} \]

where the quantities \( S_{1}, S_{2}, Sm_{1} \) and \( Sm_{2} \) are introduced for ease of notation. With (14)-(17) the overall balances, eqs (11)-(13) can be rewritten as

\[ \sum_{i=1}^{\infty} \omega_{i} = \sum_{i=1}^{\infty} \omega_{i} = \sum_{i=1}^{\infty} \omega_{i} \]

where \( v \) is defined as

\[ v = x_{WF} \]

(21)
Appendix B: Equilibrium molar fractions in aqueous methanolic formaldehyde solutions

The set of eqs (18)-(21) can easily be solved for $x_{WF}$, $x_M$ and $x_{W}$ by iteration on $v$, where $v$ is limited to $0 \leq v < 1$. The other molar fractions, $x_F$, $x_{WF}$ $(i \geq 2)$ and $x_{MF}$ $(i \geq 1)$, can be obtained from (6)-(10) straight forward. Figure 1 illustrates the smooth variation of the ratio $v$ with the overall formaldehyde molar fraction. Here, $K_1$ was taken from Winkelman et. al (2002), $K_2$, $K_3$ and $KM_2$ were taken from Hahnenstein et. al (1995), and $KM_1$ was obtained by multiplying $K_{WM}$ (Hahnenstein et. al, 1995) and $K_1$, where $K_{WM}$ the equilibrium constant is of the reaction $\text{CH}_2(\text{OH})_2 + \text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_2\text{OH} + \text{H}_2\text{O}$.

Simplifications

1. Free formaldehyde is not important

If the very small molar fraction of free formaldehyde is not important, then eq (18) reduces to

$$x_{WF} = \frac{\bar{x}_F(1 + Sm) - Sm\bar{x}_M}{S(1 - \bar{x}_F)(1 + Sm)} .$$

The system now consists of eqs (19)-(22), and can be solved in the same way as before, by iteration on $v$.
Appendix B: Equilibrium molar fractions in aqueous methanolic formaldehyde solutions

2. No methanol present
If the mixture does not contain any methanol then of course \( \tilde{x}_M, x_M \) and \( x_{MF^i} (i \geq 1) \) all are zero, and eqs (18) and (20) for obtaining \( x_{WF_1} \) and \( x_W \) reduce to

\[
x_{WF_1} = \frac{(K_1 \tilde{x}_F - v)}{K_1(1-\tilde{x}_F)S_2},
\]
\[
x_W = \tilde{x}_W + (\tilde{x}_W S_2 - S_1)x_{WF_1}.
\]

For this case, Fig. 2 illustrates the relative amount of methylene glycol with increasing overall formaldehyde content in aqueous solutions. The figure shows that at low concentrations, say below 1 mmol/l, virtually all the formaldehyde is present as methylene glycol, and the amount of poly oxymethylene glycols is negligible.

![Fig. 2. The relative amount of methylene glycol at temperatures of 300, 320 and 340 K.](image)

If also the very small molar fraction of free formaldehyde is not important, p.e. in the calculation of the viscosity (see Appendix A), then the ratio \( v \) can be obtained from the cubic equation

\[
a_1v^3 + a_2v^2 + a_3v + a_4 = 0,
\]

with the coefficients

\[
a_1 = K_3(K_3 - K_2)(1-2\tilde{x}_F),
\]
\[
a_2 = K_3\tilde{x}_F(1-K_3) + (3\tilde{x}_F - 2)(K_3 - K_2),
\]
\[
a_3 = 1-2\tilde{x}_F(1-K_3),
\]
\[
a_4 = -\tilde{x}_F.
\]
The physically significant root of eq (24) can easily be identified: either the cubic has only one real root, or the cubic has only one root in the correct region, i.e., $0 \leq \nu < 1$. The true molar fractions of water and methylene glycol are now obtained from

$$x_w = 1 - \frac{\tilde{x}_F}{1 - \tilde{x}_F} \frac{(1 - K_3 \nu)^2 + K_2 \nu(1 - K_3 \nu)}{(1 - K_3 \nu)^2 + K_2 \nu(2 - K_3 \nu)},$$

(30)

$$x_{WFG} = x_w \nu.$$

(31)

A further remark: if the overall molar fractions of formaldehyde and water are exactly equal, i.e. $\tilde{x}_F = \tilde{x}_w = 0.5$, then the cubic equation (25) degenerates to a quadratic one in $\nu$, and true molar fractions of water and methylene glycol can be obtained directly from

$$x_{WFG} = \frac{1}{1 + 2 \sqrt{K_2 + K_3}},$$

(32)

$$x_w = 1 - x_{WFG} \left(1 + \sqrt{K_2}\right).$$

(33)
Appendix C: The reaction order of formaldehyde in the hydration.

Appendix C

The reaction order of formaldehyde in its hydration reaction.

Method

The measurements described in Chapter 4 can be used to obtain the reaction order of formaldehyde in the hydration, as well as the reaction rate constant. Note that the experimental conditions and measured data allowed for the calculation of the interface concentrations and the enhancement factors, i.e. the gradients at the interface, of formaldehyde and methylene glycol without any information on the kinetics of the hydration reaction. These quantities are indexed here as observed.

To establish the reaction order of formaldehyde in the hydration, the equations for diffusion with parallel reaction in the liquid film are used

\[
D_F \frac{d^2 C_F}{dx^2} = R_F \quad (0 \leq x \leq \delta),
\]

\[
D_{MG} \frac{d^2 C_{MG}}{dx^2} = -R_F \quad (0 \leq x \leq \delta),
\]

with the boundary conditions

\[
(C_F)_{x=0} = (C_{F,IF})_{observed}, (C_{MG})_{x=0} = (C_{MG,IF})_{observed},
\]

\[
(C_F)_{x=\delta} = \bar{C}_F, (C_{MG})_{x=\delta} = \bar{C}_{MG}.
\]

Here, the rate of the reaction is written as

\[
R_F = k_b(C_F)^{n_F} - k_d C_{MG},
\]

where \( n_F \) denotes the reaction order of formaldehyde.

The additional condition

\[
\left( \frac{dC_F}{dx} \right)_{x=0} = \left( \frac{dC_F}{dx} \right)_{x=0, observed},
\]

allows the determination of the reaction rate constant, \( k_b \). The gradient of methylene glycol at the interface is not independent, but is determined by the one of formaldehyde and the interface concentrations. This can easily be seen by adding eqs (1) and (2), integrating twice, and applying boundary conditions (3) and (4), giving
Appendix C: The reaction order of formaldehyde in the hydration.

\[ C_{MG} = C_{MG,IF} + v(C_{F,IF} - C_{F}) - \frac{X}{\delta} [v(C_{F,IF} - \bar{C}_F) + C_{MG,IF} - \bar{C}_{MG}], \]  
\[ (\frac{dC_{MG}}{dx})_{x=0} = -v(\frac{dC_F}{dx})_{x=0} - \frac{1}{\delta} [v(C_{F,IF} - \bar{C}_F) + C_{MG,IF} - \bar{C}_{MG}]. \]  

Thus, for individual experiments we have no further information available to determine \( n_F \). Therefore, the following strategy was adopted. For a given value of \( n_F \), the reaction rate constants, \( k(n_F) \), were calculated for all experiments by solving eqs (1)-(7) (see below). Next, the individual rate constants were fitted to an Arrhenius type expression

\[ \hat{k}(n_F) = k_c e^{-E/RT} \]  

and the mean absolute relative residual, \( marr \), of the reaction rates was calculated

\[ marr = \frac{\sum_{i}^{all} \left| \frac{\hat{k}(n_F) - k(n_F)}{k(n_F)} \right|}{marr}. \]

This procedure was repeated for \( n_F \) values ranging from 0.0 to 2.0.

**Analytical and approximate analytical solutions**

In general, the equations (1)-(7) can be solved numerically only. However, an approximated analytical solution for the enhancement factor can be obtained by linearization of \( (C_F)^{n_F} \) according to 2\((C_{F,IF})^{n_F-1} - (n_F+1) \). Argument for this linearization is found in the solution for irreversible \( n \)th order kinetics, which, to a good approximation, equals the solution for first order kinetics, provided that the reaction rate constant, \( k \), is replaced by \( 2kC_{IF}^{n_F-1} / (n_F+1) \) (Westerterp, Van Swaaij & Beenackers, 1984). This way, the enhancement factor is very similar to the analytical solution obtained by Winkelman & Beenackers (1993) for first order reversible reactions,

\[ E_F = 1 + \frac{(1 - \tanh[\phi]) (K^{++} - \bar{C}_F) - \bar{C}_{MG}) + K\bar{C}_F - \bar{C}_{MG} (1 - \frac{1}{\cosh[\phi]})}{(K^{++}) \frac{\tanh[\phi]}{\phi}}, \]  

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Appendix C: The reaction order of formaldehyde in the hydration.

however, here with

\[
\phi' = \delta \sqrt{\frac{k'(K' + v)}{D_F K'}} ,
\]

(12)

\[
k' = \frac{2k_h}{n_v + 1} (C_{F,IF})^{n_F - 1} ,
\]

(13)

\[
K' = K + \frac{k'}{k_d} \left( \frac{2k_h}{(n_F + 1)k_d} \right) (C_{F,IF})^{n_F - 1} .
\]

(14)

For a given value of \( n_F \), the reaction rate constants were obtained from eqs (11)-(14) iteratively, using the experimental data and the observed values of the formaldehyde enhancement factors. The simple secant iteration method proved adequate for this purpose.

Note that for a first order reaction in formaldehyde, i.e. \( n_F = 1 \), eqs (11)-(14) represent the exact analytical solution. The only other case that allows for an exact solution is the zero order reaction, \( n_F = 0 \), where the enhancement factor is given by

\[
(E_F)_{n_F=0} = 1 + \frac{1}{\cosh(\phi_{n_F=0})} \left( \frac{k_h}{k_d} - \frac{C_{MG}}{C_{F,IF} - C_F} \right) \left( 1 - \frac{\tanh(\phi_{n_F=0})}{\phi_{n_F=0}} \right) \frac{C_{MG,IF} - C_{MG}}{C_{F,IF} - C_F} .
\]

(15)

where

\[
\phi_{n_F=0} = \delta \sqrt{\frac{k_d}{D_{MG}}} .
\]

(16)

**Numerical solution**

Equation (1), with \( R_F \) given by (5), \( C_{MG} \) by (7), and the boundary conditions by (3), (4) and (6), was solved for the formaldehyde concentration profile and the reaction rate constant simultaneously by replacing the differential equation by finite difference equations on a grid of mesh points on the interval \( 0 \leq x \leq \delta \). Here, \( (C_F)_j \) denotes \( C_F \) at mesh point \( j \), i.e. at \( x = j(\Delta x) \), where \( j = 1 \cdots N \) and \( (\Delta x) = \delta / N \).

A finite difference approximation of eq (1) with second order accuracy reads

\[
D_F \frac{(C_F)_{j+1} - 2(C_F)_j + (C_F)_{j-1}}{(\Delta x)^2} = (R_F)_j \quad (j = 1 \cdots N - 1) .
\]

(17)
Appendix C: The reaction order of formaldehyde in the hydration.

The boundary conditions (3) and (4) give two more equations

\[(C_F)_0 = C_{F,IF}, \quad (C_F)_N = \overline{C}_F.\]  

An additional equation is obtained from a second order Taylor series approximation of \((C_F)_1:\)

\[(C_F)_1 = (C_F)_0 + (\Delta x)\left(\frac{dC_F}{dx}\right)_0 + \frac{(\Delta x)^2}{2}\left(\frac{d^2C_F}{dx^2}\right)_0.\]  

The second derivative in (20) is equal to \((R_F)_0 / D_F,\) see eq (1), while the first derivative is set equal to the observed gradient at the interface.

The \(N + 2\) equations (17)-(20) can be solved for the unknowns \(k_h\) and \((C_F)_j (j = 0 \cdots N).\)

Because of the nonlinearity in the reaction rates \((R_F)_j\) Newton-Raphson iteration was used. For this purpose, the equations, labeled by \(F_j,\) are written as

\[F_1 = (C_F)_1 - (C_F)_0 - (\Delta x)\left(\frac{dC_F}{dx}\right)_{x=0,\text{observed}} - \frac{(\Delta x)^2}{2} \frac{(R_F)_0}{D_F} = 0,\]  
\[F_0 = (C_F)_0 - C_{F,IF} = 0,\]  
\[F_j = (C_F)_j - 2(C_F)_j + (C_F)_{j+1} - \frac{(\Delta x)^2}{D_F}(R_F)_j = 0 \quad (j = 1 \cdots N - 1),\]  
\[F_N = (C_F)_N - \overline{C}_F = 0.\]

The vector of unknowns \(y = [k_h, (C_F)_0, \cdots, (C_F)_N]^T\) is updated with a correction \(\Delta y,\) i.e. \(y_{\text{new}} = y_{\text{current}} + \Delta y,\) until convergence is achieved, where the vector of corrections \(\Delta y\) is obtained from the matrix equation

\[\sum_{k=1}^{N} \frac{\partial F_j}{\partial y_k} \Delta y_k = -F_j \quad (j = -1 \cdots N).\]

Results

The calculated \(marr\) data from eq (10), obtained with the approximate analytical solution and with the numerical method, are shown in Fig. 1 below as a function of the reaction order of formaldehyde, \(n_F.\) The data show a clear minimum around \(n_F = 1,\) allowing the conclusion that the hydration is indeed of the first order in formaldehyde.
A second conclusion is that the results obtained with the approximate analytical solution method are virtually identical to those obtained from the numerical method. Therefore, at least at the circumstances considered here, the approximate analytical method is suitable for calculating mass transfer enhancement factors.

Fig. 1. Marr of the reaction rate constants, see eq (10), vs. the order of formaldehyde in the hydration. Line: numerical solution; symbols: approximate analytical solution.