THERMODYNAMICS AND MOLECULAR-SCALE PHENOMENA

Density of solutions of formaldehyde in water and alcohols

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Abstract

Formaldehyde is an important chemical that is mostly handled in aqueous solutions, which generally also contain methanol; furthermore, also solutions of formaldehyde in other alcohols are used. The density of these solutions is an important thermophysical property. The available models of the density of formaldehyde-containing solutions, however, all have shortcomings, such as a poor accuracy or a limited range of applicability. Therefore, in the present work, a new model of the density in systems of the type (formaldehyde + water + alcohol) was developed. The alcohols that are presently included in the new model are methanol, 1-propanol, and isoprenol; an extension to other alcohols is straightforward. The model was developed using literature data and extensive new density data measured in this work covering binary, ternary, and quarternary solutions of formaldehyde in water, methanol, 1-propanol, and isoprenol at temperatures of $283 - 333$ K and formaldehyde concentrations of $0.06 - 0.30$ g g^{-1}.

KEYWORDS
alcohols, density modeling, experimental density, formaldehyde solutions, isoprenol

1 | INTRODUCTION

Formaldehyde is an important and versatile chemical, which is used in many value-added chains, such as in the production of resins.[1,2] Formaldehyde is highly reactive and is therefore most commonly stored and handled in aqueous solutions, which generally also contain methanol. The methanol may stem from the formaldehyde production process, but is also added as a stabilizer to prevent paraformaldehyde precipitation.[1,2] In these solutions, the formaldehyde is mainly bound in its oligomers with water and the alcohol, that is, in poly-oxymethylene glycols and polyoxymethylene hemiformals, whereas monomeric formaldehyde is only present in very low amounts.[1,3] Other systems of the type (formaldehyde + water + alcohol), with alcohols such as butynediol and isoprenol, are also important in industrial chemistry.[4–7]

The specific density (for brevity denoted as density throughout this work) is an important basic thermophysical property and is needed at many stages in the design and operation of industrial processes as well as in research. Due to the formation of the formaldehyde oligomers, modeling the density of formaldehyde-containing solutions is challenging, so only few models are available in the literature. These models are briefly introduced in the following.

Most of the literature models have the same structure, which is given in Equation (1):

$$\left(\rho/\text{kg m}^{-3}\right) = a + \left(\widetilde{x}_{\text{FA}}/\text{g g}^{-1}\right)\left[b + c(T/\text{K})\right] + \left(\widetilde{x}_{\text{ME}}/\text{g g}^{-1}\right) \times \left[d + e(T/\text{K})\right] \quad (1)$$

where ρ is the density of the solution, $\widetilde{x}_{\text{FA}}$ and $\widetilde{x}_{\text{ME}}$ are the overall mass fractions of formaldehyde and methanol, and T is the temperature. Overall concentrations are obtained by theoretically decomposing all occurring formaldehyde oligomers to their building blocks formaldehyde, water, and the respective alcohols. $a-e$ are model parameters, which differ between the models conforming to Equation (1).

These models include correlations reported in *Ullmann's Encyclopedia of Industrial Chemistry*,[1] in the *Kirk-Othmer Encyclopedia of Chemical Technology*,[2] and in ASTM D2380–04,[8] as well as correlations of Winkelman and Beenackers,[9] Soboleva et al.,[10] Walker,[3] Natta and Baccaredda,[11] and Homer.[12] All of these models can only be applied to solutions of (formaldehyde + water) and (formaldehyde + water + methanol). In most cases, they also have further shortcomings, such as a poor accuracy or a limited range of validity regarding temperatures or concentrations. The model parameters $a–e$ and the respective ranges of validity of the models conforming to Equation (1) are given in the Supporting Information.

The *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*[13] include a correlation that expresses the density of solutions of (formaldehyde + water) as a third order polynomial of the overall formaldehyde mass fraction. The correlation can, however, only be applied at 288 K, which drastically limits its usage. Further details are given in the Supporting Information.

Ott[14] proposed a model of the density of solutions of (formaldehyde + water + methanol) based on the model of Spencer and Danner,[15] which is a combination of a modified version of the Rackett equation[16] for pure components and the mixing rules of Chueh and Prausnitz.[17] The model was basically chosen by Ott,[14] as it enables a simple usage in process simulators. Details on the model are given in the Supporting Information. The model can be extended to also include other alcohols than methanol, but this requires knowledge of the true species distribution in the solution, that is, the concentrations of all components including the formaldehyde oligomers in the chemical equilibrium must be known. This information is available for many practically relevant formaldehyde-containing solutions,[18,19] but by far not for all. Other model parameters can be estimated using group-contribution methods. This makes the model of Ott[14] predictive, but also results in a rather poor accuracy. Information on the true species distribution in a formaldehyde-containing solution can be obtained from a chemical equilibrium model, which is demonstrated in the Supporting Information. Calculating the true species distribution also adds further complexity to the density model.

Hasse and Maurer[20] and Hahnenstein et al.[21] proposed a model based on group contributions to calculate the volume of formaldehyde-containing solutions in their works on the kinetics of the oligomerization reactions of formaldehyde with water and methanol. The model was, however, only used to calculate density changes over time during reaction kinetic experiments. While it could in principle also be used to calculate the density itself, the model parameters needed for that were not given in the respective works. Also, as for the model of Ott,[14] knowledge of the true species distribution in the solution would be needed for using the group contribution-based model.

The most recent model of the density of formaldehyde-containing solutions stems from Bai et al.[22] It is also based on knowledge of the true species distribution and relies heavily on COSMO-RS[23,24] calculations, which makes it complicated to use. This complexity does, however, not pay off, as the accuracy of the model is even slightly worse than that of other simple empirical models, such as the model of Winkelman and Beenackers.[9] The model of Bai et al.[22] was therefore not further considered in this work.

To overcome the shortcomings of the previous models, a new model for the calculation of densities of solutions containing formaldehyde, water, and alcohols was developed in the present work. The model is able to describe the available experimental data very well and covers a wide range of temperatures and concentrations. The alcohols that are presently included in the model are methanol, 1-propanol, and isoprenol, but the model can easily be extended to also include other alcohols. 1-propanol and isoprenol were chosen here besides methanol, as a chemical equilibrium model of the oligomerization reactions of formaldehyde with these alcohols is available,[18,19] which is needed for applying the model proposed by Ott.[14]

The new model was developed using comprehensive experimental data from the literature as well as extensive new experimental data measured in this work. The literature data comprise liquid densities of the formaldehyde-free binary systems (water + methanol) and (water + 1-propanol), as well as the formaldehyde-containing systems (formaldehyde + water) and (formaldehyde + water + methanol). For the present study, the data on the latter two systems were thoroughly compiled and evaluated for the first time. The new data of this work comprise densities of binary, ternary, and quaternary solutions containing formaldehyde (CH_2O, FA), water (H_2O, WA), methanol (CH_3OH, ME), 1-propanol ($CH_3CH_2CH_2OH$, PR), and isoprenol ($CH_2=C(CH_3)CH_2CH_2OH$, MBE), covering temperatures ranging from 283 to 333 K, overall formaldehyde mass fractions ranging from 0.06 to 0.30 g g^{-1}, and overall alcohol mass fractions ranging from 0.22 to 0.85 g g^{-1}. To the best of our knowledge, densities of formaldehyde solutions containing other alcohols than methanol were studied in the present work for the first time. An overview of the literature data and of the data of this work on the density of formaldehyde-containing solutions is given in Table 1. An Excel file of the data is attached to the Supporting Information. All measurements were carried out at ambient pressure, so the pressure is not specified explicitly.

2 | EXPERIMENTAL SECTION

2.1 | Chemicals

Paraformaldehyde (≥ 0.95 g g^{-1}) and isoprenol (≥ 0.994 g g^{-1}) were purchased from Sigma-Aldrich. Methanol (≥ 0.998 g g^{-1}), ethanol (≥ 0.999 g g^{-1}), and 1-propanol (≥ 0.999 g g^{-1}) were purchased from Merck KGaG. All chemicals were used without further purification. Water was deionized and purified with a Milli-Q Reference A+ purification system by Merck Millipore.

Stock solutions of (formaldehyde + water) and (formaldehyde + isoprenol) were prepared by dissolving paraformaldehyde powder in water or isoprenol at elevated temperatures as described in more detail elsewhere.[19] The overall formaldehyde mass fraction in these stock solutions was determined with a relative uncertainty of 2% by the Na$_2$SO$_3$ titration method[3] using an OMNIS Titrator by Metrohm.

TABLE 1 Overview of the available experimental data on the density of solutions of formaldehyde in water and alcohols

Solution	T/K	$\tilde{x}_{FA}/g\,g^{-1}$	$\tilde{x}_{ME}/g\,g^{-1}$	$\tilde{x}_{PR}/g\,g^{-1}$	$\tilde{x}_{MBE}/g\,g^{-1}$	Data points	Refs
(FA + WA)	288	0.10–0.36				14	[25]
	288–298	0.06–0.43				16	[26]
	288–308	0.02–0.17				15	[27]
	289	0.02–0.39				17	[28][a]
	291	0.02–0.38				9	[29]
	291	0.05–0.50				10	[11]
	291	0.37				1	[30]
	291–313	0.09–0.37				15	[22]
	292	0.01–0.40				40	[31][a]
	293–313	0.03–0.38				45	[32]
	293–383	0.05–0.90				56	[10][a]
	298	0.37–0.38				9	[3]
	283–333	0.09–0.27				12	This work
(FA + WA + ME)	288	0.10–0.30	0.05–0.50			14	[12]
	288	0.10–0.40	0.02–0.20			136	[25]
	288–298	0.26–0.42	0.02–0.20			58	[26]
	291	0.03–0.45	0.05–0.90			63	[11]
	291–313	0.10–0.30	0.18–0.73			12	[22][a]
	291	0.37	0.05–0.15			3	[30]
	298–338	0.37–0.50	0.01–0.15			1358	[3][a]
	283–333	0.06–0.18	0.33–0.67			16	This work
(FA + WA + PR)	283–333	0.06–0.18		0.33–0.67		16	
(FA + MBE)	283–333	0.15–0.30			0.70–0.85	8	
(FA + WA + MBE)	283–333	0.18–0.30			0.56–0.69	7	
(FA + WA + ME + PR)	298–333	0.06–0.18	0.16–0.53	0.17–0.33		9	
(FA + WA + ME + MBE)	298–333	0.10–0.15	0.17–0.52		0.22–0.35	9	
Total	283–383	0.01–0.90	0.01–0.90	0.17–0.67	0.22–0.85	1968	

Abbreviations: FA, formaldehyde; MBE, isoprenol; ME, methanol; PR, 1-propanol; WA, water.

[a]Some or all of the data were not considered in the present work. Explanations are given in the Supporting Information.

[Correction added on 18 February 2022, after first online publication: Table 1 corrected.]

2.2 | Experimental procedure

The formaldehyde-containing samples were prepared gravimetrically by mixing stock solutions of (formaldehyde + water) and (formaldehyde + isoprenol) with pure water, methanol, 1-propanol, and isoprenol. The relative uncertainty of the overall mass fractions in these solutions is 2% and stems mainly from the uncertainty in the determination of the overall formaldehyde mass fraction of the stock solutions.

Prior to the actual measurements, the samples were treated as follows: for experiments at temperatures of 298 K and above, first, the samples were equilibrated in a thermostated water bath for at least 14 h to ensure that the chemical equilibrium was established. Second, the samples were degassed at the same temperature in a thermostated ultrasonic bath for at least 15 min through a small cannula inserted in the septum of the sample vials. The shift of the concentrations in the samples resulting from the degassing is negligible

and is included in the already stated relative uncertainty of the overall concentrations. After the degassing, the samples were once again stored in the thermostated water bath for at least 1 h prior to the first density measurement. In contrast, for experiments at 283 K, the samples were degassed at room temperature for at least 15 min before they were stored in the thermostated water bath for at least 2 weeks and were not again degassed prior to the density measurements. This approach was taken, as the ultrasonic bath could not be cooled down below room temperature. Independent of the temperature of the experiments, the samples were kept in the thermostated water bath at all times during the actual density measurements.

The experiments were performed at ambient pressure with an Anton Paar DMA 5000 M oscillating tube densimeter. After each density measurement, the oscillating tube was cleaned with pure water and ethanol and was dried with dehumidified air. Each density measurement was repeated three times. The relative standard deviation of the three results was generally less than 0.01%. Only the mean

value of the three results is reported in the present work. At the beginning of each isothermal series of measurements, the density of degassed pure water was measured at the studied temperature and compared to a reference value obtained from the IAPWS-95 equation of state.[33] The relative deviation between the measured density of pure water and the reference value was always less than 0.01%. Overall, the relative experimental uncertainty of the density measurements is less than 0.05%. The absolute uncertainty of the temperatures reported in this work is 0.15 K, which comprises uncertainties of the temperature during equilibration in the thermostated water bath prior to the density measurements and uncertainties of the temperature control of the densimeter.

3 | MODELING

The new model of this work is an empirical correlation of the density based on overall concentrations and is given in Equation (2):

$$\rho = \sum_i \widetilde{x}_i \rho_i(T) + \frac{1}{2} \sum_i \sum_j \widetilde{x}_i \widetilde{x}_j a_{i,j} \tag{2}$$

where i and j stand for overall components, $\widetilde{x}_i$ is the overall mass fraction of i, $\rho_i(T)$ is the pure component density of i, and $a_{i,j}$ are adjustable parameters that describe binary interactions between the overall components in the solution. The temperature dependence of the model stems only from the pure component densities. The interaction parameters were chosen to be temperature-independent, which was sufficient to accurately describe the available experimental data. There is only one adjustable interaction parameter between the components i and j, that is, $a_{i,j} = a_{j,i}$, and interactions of components with themselves are always zero, that is, $a_{i,i} = 0$.

The model has a different structure than the previous literature models. It can be interpreted as follows: the first sum in Equation (2) resembles the density of an ideal mixture of the overall components, and the second sum resembles an excess density. The terms "ideal" and "excess" should, however, not be over-interpreted. We do not intend to formally define an ideal mixture or excess properties here, but the analogy with the formal concept is convenient. Due to its structure, the new model offers some advantages over the previous models: it is easy to use, in the limiting cases of pure components, the model yields the respective pure component densities, it can easily be extended to included other alcohols, and binary interactions in the solutions can be taken into account in a straightforward way via the interaction terms $\widetilde{x}_i \widetilde{x}_j a_{i,j}$.

In the present study, the new model was parameterized for solutions containing formaldehyde, water, methanol, 1-propanol, and isoprenol. Other alcohols can be included in the model by taking the following two-step approach: in a first step, the pure component density of the alcohol, which is well known in most cases, is included in the ideal mixture term of Equation (2). At this stage, the model can already be used to obtain fair predictions of the density of solutions containing the new alcohol. Then, in a second step, to further improve the model accuracy, the binary interaction parameters $a_{i,j}$ in the excess term of Equation (2) are fitted to experimental density data on solutions containing the alcohol. As $a_{i,j}$ is temperature-independent, a minimum of only one experimental data point for the density of a solution containing the components i and j is needed to determine $a_{i,j}$.

Even though the model was mainly developed for calculating densities of formaldehyde-containing solutions, also formaldehyde-free solutions can be described reasonably well by the model. This is, however, not the main focus of this work and is therefore only briefly shown in the Supporting Information.

In the following, the correlations of the pure component densities $\rho_i(T)$ are given, and the determination of the adjustable interaction parameters $a_{i,j}$ is discussed.

3.1 | Pure component densities

The density of pure water was correlated using the DIPPR equation[34]:

$$\left(\rho_{WA}/\text{kg m}^{-3}\right) = \left(M_{WA}/\text{g mol}^{-1}\right)\left[A_{WA} + B_{WA}\tau^{1/3} + C_{WA}\tau^{2/3} + D_{WA}\tau^{5/3} \right.$$
$$\left. + E_{WA}\tau^{16/3} + F_{WA}\tau^{43/3} + G_{WA}\tau^{110/3}\right]$$
$$\text{with} \quad \tau = 1 - \frac{T}{T_{c,WA}} \tag{3}$$

[Correction added on 18 February 2022, after first online publication: Equation 3 format corrected.]
where $M_{WA} = 18.01528 \text{ g mol}^{-1}$ is the molar mass and $T_{c,WA} = 647.096 \text{ K}$ is the critical temperature of water. The parameters in Equation (3) are $A_{WA} = 17.874$, $B_{WA} = 35.618$, $C_{WA} = 19.655$, $D_{WA} = -9.1306$, $E_{WA} = -31.367$, $F_{WA} = -813.56$, and $G_{WA} = -17421000$. They were adopted from the DIPPR database (version of May 2019).[34]

The densities of pure methanol and 1-propanol were correlated using Equation (4), which is included in *VDI Wärmeatlas*[35]:

$$\left(\rho_i/\text{kg m}^{-3}\right) = A_i + B_i\tau^{0.35} + C_i\tau^{2/3} + D_i\tau + E_i\tau^{4/3}, \ i = \text{ME, PR}$$
$$\text{with} \quad \tau = 1 - \frac{T}{T_{c,i}} \tag{4}$$

where $T_{c,i}$ is the critical temperature of component i and A_i, B_i, C_i, and D_i are model parameters, which were adopted from *VDI Wärmeatlas*[35] and are given in Table 2.

The density of pure isoprenol was correlated using a modified version of the Rackett equation[36]:

$$\left(\rho_{MBE}/\text{kg m}^{-3}\right) = \frac{A_{MBE}}{B_{MBE}^{1 + \left[1 - \frac{(T/K)}{C_{MBE}}\right]^{D_{MBE}}}} \tag{5}$$

where $A_{MBE} = 0.2066$, $B_{MBE} = 0.01411$, $C_{MBE} = 609.8$, and $D_{MBE} = 0.07232$ are model parameters, which were fitted in the present work to experimental data from the literature and new experimental data of this work. Details are given in the Supporting Information.

A correlation of the density of pure formaldehyde based on experimental data is available in the DIPPR database (version of May

TABLE 2 Parameters adopted from *VDI Wärmeatlas*[35] for the calculation of pure component densities using Equation (4)

Component	A	B	C	D	E	T_c / K
Methanol	282	164.7611	2257.7678	−3545.6923	1929.7376	513.38
1-Propanol	274	816.2709	−549.2099	696.9841	−232.0820	536.75

TABLE 3 Interaction parameters $a_{i,j}$/kg m^{-3}

	j				
i	**FA**	**WA**	**ME**	**PR**	**MBE**
FA		−8.6	−205.8	−240.2	−165.6
WA	−8.6		72.6	23.6	
ME	−205.8	72.6			
PR	−240.2	23.6			
MBE	−165.6				

Abbreviations: FA, formaldehyde; MBE, isoprenol; ME, methanol; PR, 1-propanol; WA, water.

2019).[34] However, using this correlation yielded poor results in our calculations, which is not surprising, as formaldehyde is mainly bound in its oligomers with water and the alcohols.[3,19] Therefore, a separate correlation of the density of pure formaldehyde in systems of the type (formaldehyde + water + alcohol) was developed in the present work, which is given in Equation (6):

$$(\rho_{FA}/\text{kg m}^{-3}) = A_{FA} + B_{FA}(T/\text{K}) \tag{6}$$

where $A_{FA} = 1507.8$ and $B_{FA} = -0.6682$ are model parameters. These model parameters as well as the interaction parameter between (formaldehyde + water), $a_{FA,WA}$, were fitted simultaneously to all available experimental data on the density of solutions of (formaldehyde + water) shown in Table 1. Data on other formaldehyde-containing systems were not used in this step, as this would have resulted in a slightly worse fitting result for the system (formaldehyde + water), which is the most important formaldehyde-containing system. The fitting procedure was as follows: the overall composition of the solutions and the temperature were specified as input and the densities were calculated using Equation (2). The model parameters were then determined by minimizing the mean absolute percentage deviation (MAPD):

$$\text{MAPD} = \frac{100}{M} \sum_{m=1}^{M} \left| \frac{\rho_m^{\text{calc}} - \rho_m^{\text{exp}}}{\rho_m^{\text{exp}}} \right| \tag{7}$$

where ρ_m^{exp} and ρ_m^{calc} are the experimental and calculated density of a data point m, respectively, and M is the total number of data points that were considered.

3.2 | Interaction parameters

Ten binary interaction parameters were determined to describe the interactions between the five overall components formaldehyde, water, methanol, 1-propanol, and isoprenol. The interaction parameter between (formaldehyde + water), $a_{FA,WA}$, was fitted simultaneously with the correlation of the density of pure formaldehyde as described earlier. The remaining interaction parameters can be split into two groups: those between formaldehyde and the alcohols, that is, $a_{FA,ME}$, $a_{FA,PR}$, and $a_{FA,MBE}$, and those without formaldehyde, that is, $a_{WA,ME}$, $a_{WA,PR}$, $a_{WA,MBE}$, $a_{ME,PR}$, $a_{ME,MBE}$, and $a_{PR,MBE}$.

In a first step, the interaction parameters without formaldehyde were determined. The interaction parameters between (isoprenol + water), (isoprenol + methanol), and (isoprenol + 1-propanol) were set to zero, that is, $a_{WA,MBE} = a_{ME,MBE} = a_{PR,MBE} = 0$, as there were too few experimental densities of isoprenol-containing solutions available to confidently determine these parameters. The interaction parameters between (water + methanol) and (water + 1-propanol) were fitted to literature data on the respective binary systems, using the same fitting procedure as described above. The interaction parameters between (methanol + 1-propanol) were set to zero, as the available literature data indicated that the excess density between the two components is negligible. More details are given in the Supporting Information.

In a second step, the remaining interaction parameters between formaldehyde and the alcohols were fitted to all available experimental data on the density of binary and ternary solutions containing formaldehyde and the respective alcohol shown in Table 1 using the same fitting procedure as described above. The final parameters are given in Table 3.

The available experimental data of quaternary formaldehyde-containing solutions were not used in the development of the new model.

4 | RESULTS AND DISCUSSION

The experimental data of this work are given in the Supporting Information and are additionally included in the Excel file attached to the Supporting Information that contains all experimental data on formaldehyde-containing solutions shown in Table 1. This Excel file also contains densities calculated with the new density model and with the literature models considered in the present work.

This section is divided into three parts: first, trends in the experimental data are pointed out to motivate the implementation of the binary interaction terms $\tilde{x}_i \tilde{x}_j a_{i,j}$ in the new model, second, the agreement between the new model and the experimental data is shown, and third, the new model is compared to literature models.

4.1 | Motivation for implementing binary interaction terms

For binary solutions of (formaldehyde + water), the new model given in Equation (2) can be rearranged as follows:

$$\widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA} = \rho - \widetilde{x}_{FA}\rho_{FA}(T) - \widetilde{x}_{WA}\rho_{WA}(T) \tag{8}$$

The resulting Equation (8) allows the calculation of the interaction term $\widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA}$ for an experimental data point from the experimental mixture density ρ and the values for ρ_{FA} and ρ_{WA}. An interaction term of zero, that is, $\rho - \widetilde{x}_{FA}\rho_{FA}(T) - \widetilde{x}_{WA}\rho_{WA}(T) = 0$, indicates that the ideal mixture term of the new model alone would have already described the data well. Systematic deviations from zero, however, indicate that corrections to this ideal mixture term are necessary.

Figure 1 shows the interaction term $\widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA}$ for the available experimental data of binary solutions of (formaldehyde + water) as calculated using Equation (8). The model representation of the interaction term $\widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA}$, which constitutes a straight line, is also given in Figure 1.

The experimental data follow a linear trend from zero in the limiting case of pure water, that is, $\widetilde{x}_{FA}\widetilde{x}_{WA} = 0$, to slightly negative values at higher formaldehyde concentrations. This trend is described well by the model, which is a strong argument for the implementation of the binary interaction term $\widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA}$ in the model. The experimental data and the deviations between the model and the data are discussed in more detail below.

For experimental data of binary and ternary solutions containing formaldehyde, water, and the alcohols methanol, 1-propanol, and isoprenol, Equation (2) can be rearranged in a similar way to calculate the interaction terms between formaldehyde and the respective alcohols:

$$\begin{aligned}\widetilde{x}_{FA}\widetilde{x}_{j}a_{FA,j} = {} & \rho - \widetilde{x}_{FA}\rho_{FA}(T) - \widetilde{x}_{WA}\rho_{WA}(T) - \widetilde{x}_{j}\rho_{j}(T) - \widetilde{x}_{FA}\widetilde{x}_{WA}a_{FA,WA} \\ & - \widetilde{x}_{WA}\widetilde{x}_{j}a_{WA,j}\end{aligned} \tag{9}$$

where $j = $ ME, PR, or MBE. Figure 2 shows the interaction terms between (formaldehyde + methanol), (formaldehyde + 1-propanol), and (formaldehyde + isoprenol) for the available experimental data as calculated using Equation (9). The model representations of the interaction terms $\widetilde{x}_{FA}\widetilde{x}_{j}a_{FA,j}$ are also given in Figure 2.
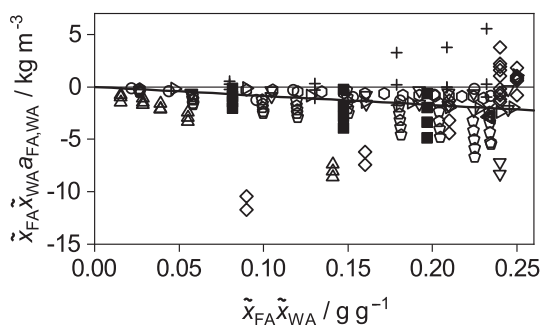
As for the solutions of (formaldehyde + water), the interaction terms of the experimental data obtained from Equation (9) show clear linear trends towards negative values. These trends are also well described by the model, which is, again, a strong argument for the implementation of the binary interaction terms in the new model.

4.2 | Comparison of experimental data and new model

In general, the density of solutions containing formaldehyde, water, and alcohols increases with increasing formaldehyde concentrations and decreases with increasing alcohol concentrations and temperatures.
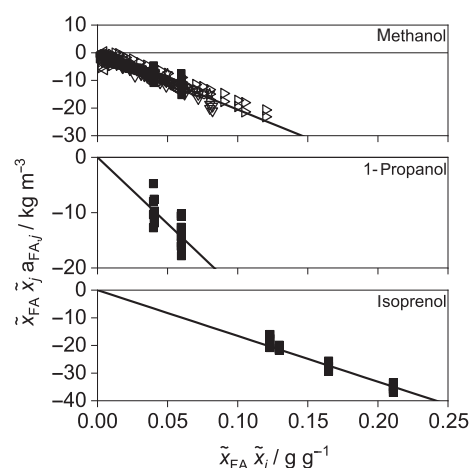

FIGURE 2 Binary interaction terms between formaldehyde and various alcohols. Experimental data: ($\triangledown$) Skelding and Ashbolt,[26] ($\triangleright$) Natta and Baccaredda,[11] ($\triangleleft$) Walker,[3] ($\circ$) *Ullmann's Encyclopedia of Industrial Chemistry*,[25] ($\times$) *Kirk-Othmer Encyclopedia of Chemical Technology*,[30] ($\star$) Homer,[12] ($\blacksquare$) this work. (——) model

FIGURE 1 Binary interaction term between (formaldehyde + water). Experimental data: ($\circ$) Auerbach and Barschall,[29] ($\triangle$) Lileev et al.,[27] ($\diamond$) Soboleva et al.,[10] ($\triangledown$) Skelding and Ashbolt,[26] ($\triangleright$) Natta and Baccaredda,[11] ($\circ$) Datar,[32] (+) Bai et al.,[22] ($\triangleleft$) Walker,[3] ($\circ$) *Ullmann's Encyclopedia of Industrial Chemistry*,[25] ($\times$) *Kirk-Othmer Encyclopedia of Chemical Technology*,[30] ($\blacksquare$) this work. (——) model
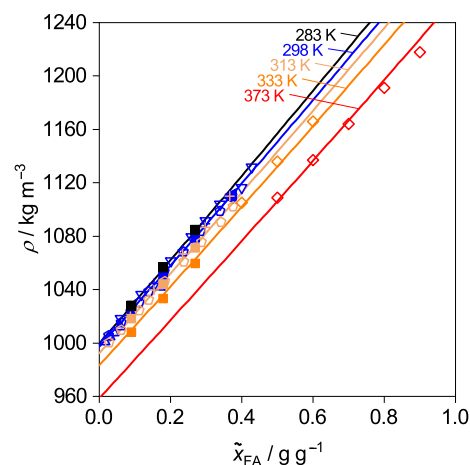
FIGURE 3 Density of solutions of (formaldehyde + water). Experimental data: ($\triangle$) Lileev et al.,[27] ($\diamond$) Soboleva et al.,[10] ($\triangledown$) Skelding and Ashbolt,[26] ($\circ$) Datar,[32] ($\triangleleft$) Walker,[3] (+) Bai et al.,[22] ($\blacksquare$) this work. (——) model

FIGURE 4 Deviations of the model of this work from the available experimental densities of solutions containing formaldehyde, water, and alcohols. Experimental data: (○) Auerbach and Barschall,[29] (△) Lileev et al.,[27] (◇) Soboleva et al.,[10] (▽) Skelding and Ashbolt,[26] (◁) Walker,[3] (▷) Natta and Baccaredda,[11] (○) Datar,[32] (+) Bai et al.,[22] (○) *Ullmann's Encyclopedia of Industrial Chemistry*,[25] (×) *Kirk-Othmer Encyclopedia of Chemical Technology*,[30] (☆) Homer,[12] (■) this work
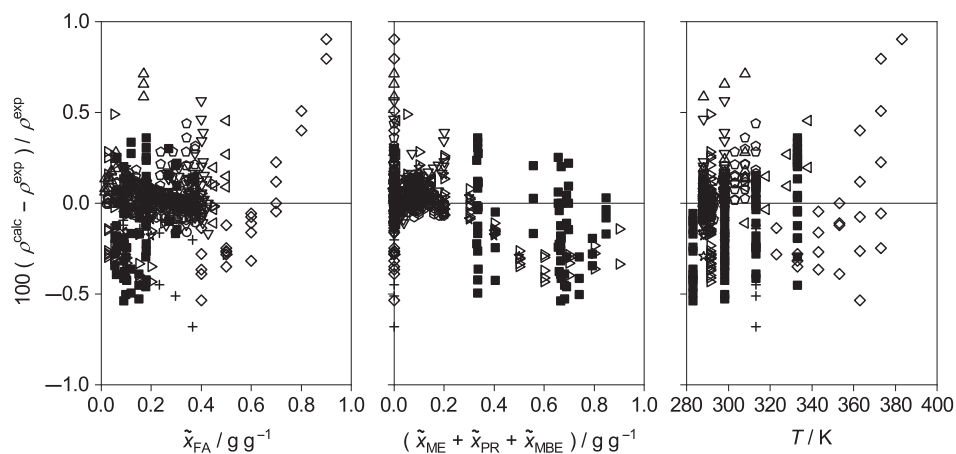

TABLE 4 MAPD of different density models for all available experimental data

Solution	WB[a]	SO[b]	UL[c]	KO[d]	OT[e]	This work
(FA + WA)	0.32	0.45	0.32	0.38	1.15	0.15
(FA + WA + ME)			0.53	0.81	0.78	0.10
(FA + WA + PR)					0.80	0.22
(FA + MBE)					4.87	0.10
(FA + WA + MBE)					0.88	0.19
(FA + WA + ME + PR)					1.37	0.22
(FA + WA + ME + MBE)					1.31	0.37

Abbreviations: FA, formaldehyde; MBE, isoprenol; ME, methanol; PR, 1-propanol; WA, water.
Notes: Literature models:
[a]Winkelman and Beenackers.[9]
[b]Soboleva et al.[10]
[c]*Ullmann's Encyclopedia of Industrial Chemistry*.[1]
[d]*Kirk-Othmer Encyclopedia of Chemical Technology*.[2]
[e]Ott.[14]

These trends are well described by the new model as shown in Figure 3 for solutions of (formaldehyde + water).

The new model is able to describe the experimental densities of the solutions of (formaldehyde + water) well over the whole temperature and concentration range. The same goes for formaldehyde solutions that also contain alcohols. This is demonstrated in Figure 4, which shows the deviations of the new model from all available experimental densities of solutions containing formaldehyde, water, and alcohols.

The majority of the deviations lies within −0.5 to 0.5%, which is a very good result considering the extensive amount of experimental data on the different systems. The data of this work show no significant biases and fit well into the existing data from the literature.

4.3 | Comparison of density models

The quality of the representation of the experimental density data in the different studied systems by the new model and by existing literature models is compared in Table 4, in which the corresponding values for the MAPD are summarized. In all cases, the MAPD was calculated using all available experimental data on the respective formaldehyde-containing solutions. As some of the considered literature models have a limited range of validity, these models had to be extrapolated to temperatures or concentrations outside of their stated ranges of validity for this comparison. Empty cells in Table 4 indicate that the models cannot be applied to the respective system. Results for the density models of Walker,[3] Natta and Baccaredda,[11] and Homer[12] as well as for the correlation included in the *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*[13] are not presented here, as these models are only valid at one specific temperature.

The models denoted as WB, SO, UL, and KO in Table 4 all have a similar accuracy, which is acceptable for many applications. The similarities between these models could be expected, as all of them conform to Equation (1) and only differ slightly in the choice of the model parameters.

The model of Ott[14] shows the largest deviations of all studied models, as most of the model parameters were not fitted to actual density data, but were instead obtained using a group-contribution method as described in the Supporting Information. However, due to

TABLE 5 MAPD of literature models with a limited range of validity when taking into account only experimental data within this range

Solution	WB[a]	UL[b]
(FA + WA)	0.14 (0.13)	0.27 (0.13)
(FA + WA + ME)		0.10 (0.07)

Abbreviations: FA, formaldehyde; ME, methanol; WA, water.

Notes: Values in parentheses indicate the MAPD of the model of this work for the same data.

Notes: Literature models:

[a]Winkelman and Beenackers.[9]

[b]*Ullmann's Encyclopedia of Industrial Chemistry*.[1]

the predictive nature of the model of Ott,[14] it is the only literature model that can readily be applied to solutions containing other alcohols than methanol, as long as information on the chemical equilibria of these solutions is available.

The model of this work shows the best accuracy among the studied models. The density of solutions containing 1-propanol and isoprenol, for which no data were previously available, is described very well and significantly better than by the model of Ott.[14] The good results for quaternary solutions of (formaldehyde + water + methanol + 1-propanol) and (formaldehyde + water + methanol + isoprenol) are even more astonishing, as the model was not fitted to data of quaternary solutions and is therefore purely predictive.

As some of the literature models had limited ranges of validity, Table 5 additionally shows the MAPD of these models for the experimental data lying within the respective ranges of validity. The MAPD of the model of this work for the same data is also given in Table 5 in parentheses.

As expected, the literature models show a smaller MAPD when they are applied to data in their respective ranges of validity. In all cases, the model of the present work still outperforms the literature models.

5 | CONCLUSIONS

The present work provides a new model for the calculation of liquid densities in systems of the type (formaldehyde + water + alcohol), which was developed using experimental data from the literature and extensive new experimental data of this work on the density of solutions containing formaldehyde, water, methanol, 1-propanol, and isoprenol.

The new model is basically an empirical correlation that describes the liquid density at ambient pressure as a function of the overall composition and the temperature. It is easy to use, more accurate than previously available literature models, and can be extended to include other alcohols than the ones studied in this work in a straightforward way. Extending the model to new alcohols is done in two steps: first, an arbitrary correlation for the temperature dependence of the density of the pure alcohol is introduced to the model; this already allows fair predictions of the density of solutions containing the new alcohol. Second, to further improve the model accuracy,

temperature-independent binary interaction parameters between the new alcohol and the other overall components are fitted to at least one data point of the density of a solution containing both the new alcohol and the respective overall component.

The new experimental data reported in this work were measured with an Anton Paar DMA 5000 M oscillating tube densimeter and cover temperatures ranging from 283 to 333 K, overall formaldehyde mass fractions ranging from 0.06 to 0.30 g g^{-1}, and overall alcohol mass fractions ranging from 0.22 to 0.85 g g^{-1}. Formaldehyde-containing solutions with other alcohols than methanol were studied here for the first time. The density data of this work therefore represent a substantial contribution to the previously existing data.

AUTHOR CONTRIBUTIONS

Maximilian Dyga: Conceptualization (equal); investigation (equal); methodology (equal); writing – original draft (equal). **Andreas Keller:** Conceptualization (equal); resources (equal). **Hans Hasse:** Conceptualization (equal); resources (equal); supervision (equal); writing – review and editing (equal).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the Supporting Information of this article.

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SUPPORTING INFORMATION

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