Vapor–Liquid Equilibrium of Formaldehyde Mixtures: New Data and Model Revision

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A physicochemical model for vapor–liquid equilibria and enthalpies in formaldehyde-containing mixtures is revised and extended using recently published NMR spectroscopic data on chemical equilibria in aqueous and methanolic formaldehyde solutions as well as new vapor–liquid equilibrium data for the system formaldehyde–water at temperatures up to 413 K (pressures up to 450 kPa), which were taken in this work with a new apparatus. Furthermore, the model is revised so that it can be extended straightforwardly to explicitly account for reaction kinetic effects based on results from other recent NMR spectroscopic studies. The model is tested over the entire temperature range (293–413 K), where reliable experimental data on vapor–liquid equilibria are available, and against calorimetric data. Typical relative deviations between experimental data and the correlation are about 5% for vapor–liquid partition coefficients and 2% for the pressure. Deviations between calculated and measured enthalpies of vaporization are generally below 2%.

Introduction

Formaldehyde is a very important chemical intermediate. It is highly reactive and therefore commonly handled in aqueous and methanolic solutions, where it forms different adducts with the solvents. For the design of separation processes, models for thermodynamic properties of these chemically reactive mixtures are needed. As the inverse rate constants of the reactions in formaldehyde-containing solutions are often of the same order of magnitude as residence times in separation equipment, reaction kinetics can have an important influence on separation processes. Common ad hoc procedures to account for reaction kinetic effects, for example, by lowering the tray efficiency, do not yield satisfactory results for processes like absorbing formaldehyde in water at room temperature. Therefore, models for thermodynamic equilibrium properties of formaldehyde-containing mixtures should be complemented by reaction kinetic models, to allow simulations of all types of separation equipment commonly used in formaldehyde processing.

In the present work, a previously reported and continuously updated physicochemical model for vapor–liquid equilibria and enthalpies in formaldehyde-containing mixtures (Maurer, 1986; Hasse et al., 1990; Hasse and Maurer, 1991a; Liu et al., 1992; for a survey comprehensive up to 1992, see Hahnenstein et al., 1994a) is revised and extended. The revision was made in order to include new information on equilibria and kinetics of chemical reactions in aqueous and methanolic formaldehyde solutions, which has recently become available (Hahnenstein et al., 1994b, 1995). Furthermore, the temperature range in which the model gives reliable results was extended on the basis of new data taken in the present work.

The equilibrium model presented here is designed so that it can be complemented straightforwardly by a reaction kinetic model. The prerequisite for such an extension is that both the equilibrium and the kinetic model are consistent. Reaction kinetics are commonly modeled using concentrations rather than activities (see, e.g., Hahnenstein et al., 1995). Equilibrium states at the end of kinetic experiments are therefore described with equilibrium constants K_x rather than with thermodynamic equilibrium constants K (using activities). Contrarily, in thermodynamic equilibrium models, K will be used rather than K_x (see, e.g., Maurer, 1986). As both types of models have to be consistent, a choice has to be made. Introducing corrections by activity coefficients does not make much sense in evaluating the often rather crude reaction kinetic information. Therefore, we decided to also use

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K_x in the equilibrium model. The numbers for K_x for the oligomer formation in aqueous and methanolic formaldehyde solutions are directly taken from the NMR spectroscopic investigation of Hahnenstein et al. (1994b). Chemical equilibria in the gas phase are described using the densimetric data of Kogan (1979b). So, true concentrations calculated with the model are in agreement with experimental evidence, and the model is suited for an extension including reaction kinetic data (Hahnenstein et al., 1995).

It should be realized, however, that the price for these benefits is the loss of thermodynamic consistency of the model. While in most applications this is not likely to cause any problems, there are algorithms that should not be used with the model, for example, a minimization of the Gibbs Energie G for simultaneous evaluation of chemical and physical equilibrium, or direct thermodynamic stability tests using derivatives of G.

The original version of the model (Maurer, 1986) described the experimental vapor–liquid equilibria at temperatures between about 323 and 373 K reliably. However, information on vapor–liquid equilibria at both lower and higher temperatures is also needed, for example, for the design of equipment for formaldehyde absorption in water at room temperature or for separations in the trioxane production at temperatures above 400 K. In previous work the temperature range was extended to 293–373 K (Hasse and Maurer, 1991a), based on data taken at 293 and 313 K. In the present work, the temperature range is extended to higher temperatures based on new vapor–liquid equilibrium data in the formaldehyde–water system at temperatures up to 413 K. These new data were taken in the present work with a vapor–liquid equilibrium apparatus, especially developed for this purpose. The new model works well over the entire range where reliable data are available (293–413 K). Deviations between measurement and calculation are typically below 5% for partition coefficients and 2% for pressures.

Models for vapor–liquid equilibria are often used in process simulators, where calculation time is an important feature. Therefore, the new model was kept as simple as possible without loosing accuracy.

For separation process simulation, besides phase equilibrium models enthalpy models are also needed. A physicochemical enthalpy model for formaldehyde-containing mixtures has previously been reported (Liu et al., 1992). In the present work that model was adapted to the modified version of the vapor–liquid equilibrium model. Based only on information already used in the vapor–liquid equilibrium model, the enthalpy model predicts calorimetric data on heats of vaporization of formaldehyde-containing solutions with relative errors typically about 5%. Deviations can be reduced further (to below 2%), when calorimetric data are used to adjust model parameters.

Chemical Reactions in Aqueous and Methanolic Formaldehyde Solutions

Only the most important chemical reactions in aqueous and methanolic formaldehyde solutions are discussed here. For a more detailed survey, see Walker (1964).

In aqueous solutions, methylene glycol ($HOCH_2OH$; here also, MG) and poly(oxymethylene) glycols [$HO(CH_2O)_iH$, $i > 1$; here also, MG_i] are formed:

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \quad \text{(I)}$$

$$HO(CH_2O)_{i-1}H + HOCH_2OH \rightleftharpoons HO(CH_2O)_iH + H_2O, \quad i > 1. \quad \text{(II)}$$

Similarly, in methanolic formaldehyde solutions hemiformal ($HOCH_2OCH_3$; here also, HF) and poly(oxymethylene) hemiformals [$HO(CH_2O)_iCH_3$, $i > 1$; here also, HF_i] are formed:

$$CH_2O + CH_3OH \rightleftharpoons HOCH_2OCH_3 \quad \text{(III)}$$

$$HO(CH_2O)_{i-1}CH_3 + HOCH_2OCH_3 \rightleftharpoons HO(CH_2O)_iCH_3 + CH_3OH, \quad i > 1. \quad \text{(IV)}$$

Chemical reactions I–IV have an essential influence on properties of aqueous and methanolic formaldehyde solutions. They have to be taken into account in thermodynamic models of phase equilibria and caloric properties of formaldehyde-containing systems.

The literature on chemical equilibria of reactions I and III (for references, see Hasse and Maurer, 1991b) shows that the concentration of monomeric formaldehyde in liquid phases is always very low. Ratios $x_{FA}/\tilde{x}_{FA}$ (true formaldehyde concentration/overall formaldehyde concentration) are typically below 0.01 in aqueous solutions and below 0.005 in methanolic solutions. In the gas phase, however, the corresponding ratios $y_{FA}/\tilde{y}_{FA}$ are typically about 0.9 (formaldehyde–water) or 0.1 (formaldehyde–methanol), respectively, showing that monomeric formaldehyde cannot be neglected in gaseous mixtures.

There is no experimental evidence for the presence of substantial amounts of poly(oxymethylene) glycols or poly(oxymethylene) hemiformals in the gas phase, so reactions II and IV only have to be considered in the liquid phase. A survey of data on equilibrium and rate constants for reaction II and IV, including extensive new equilibrium and kinetic data has recently been given (Hahnenstein et al., 1994b, 1995).

Generally, the formaldehyde oligomer concentration decreases with an increasing number i of CH_2O segments in the oligomer. In diluted aqueous and methanolic solutions, formaldehyde is almost exclusively present as methylene glycol or hemiformal, respectively. In aqueous solutions, the average number of CH_2O segments $\bar{i}$ in formaldehyde oligomers is distinctly larger than in methanolic solutions (e.g., at 293 K and $\tilde{x}_{FA} = 0.3$ mol·mol^{-1}: $\bar{i} = 2.1$ in water and $\bar{i} = 1.1$ in methanol). In the mixed solvent water–methanol, formaldehyde prefers to react with methanol (e.g., at 293 K and $\tilde{x}_{FA} = 0.3$ mol·mol^{-1}, $\tilde{x}_W = \tilde{x}_{Me} = 0.35$ mol·mol^{-1}; $x_{MG} = 0.02$ mol·mol^{-1}, $x_{HF} = 0.26$ mol·mol^{-1}). The inverse reaction rates at 293 K are about 6 min for the poly(oxymethylene) glycol formation (1 min for the degradation), but 110 h for the poly(oxymethylene) hemiformal formation (860 h for the degradation).

New Vapor–Liquid Equilibrium Apparatus and Data

Reliable data on vapor–liquid equilibria of formaldehyde-containing mixtures at elevated temperatures and pressures are needed for industrial process design, for example, triox-

ane production. Several investigations of vapor–liquid equilibria in the formaldehyde–water system at temperatures above 373 K (pressures above 100 kPa) have been reported in the literature (Blazhin et al., 1977 (isobaric data, $p_{max} = 506$ kPa); Olsson and Svensson, 1975 (isothermal data, $T_{max} = 403$ K); and Farberov and Speranskaya, 1955 (isobaric data, $p_{max} = 400$ kPa)). As these data show numerous discrepancies, and the reliability of data in the literature on formaldehyde-containing systems is often difficult to assess, new experiments were carried out in the present work.

The phase equilibrium apparatus used in the present work for measuring vapor–liquid equilibria in formaldehyde-containing systems is similar to that previously described by Hasse et al. (1990). It is a special type of thin-film evaporator, in which a rotating coil spreads the liquid feed on the inner surface of a tube, which is surrounded by a heating jacket. The liquid partially evaporates, and the coexisting phases are separated and collected in vials. With that apparatus experiments can be carried out at small evaporation ratios and high residence times, so that chemical equilibria in the liquid phase are not essentially disturbed. However, in earlier investigations a glass apparatus was used that was not suited for experiments above atmospheric pressure. Therefore, in the present work a new apparatus was built of stainless steel. It can be used for measurements up to 500 kPa. Except for the material, the detailed description of the glass apparatus given by Hasse et al. (1990) still holds. The accuracy of the experimental results is better than 0.1 K for the temperature (measured with a platinum resistance thermometer PT 100 connected to a multimeter, from Prema, Mainz, Germany) and better than 0.5 kPa for the pressure (measured with a transducer from WIKA, Klingenberg, Germany).

Formaldehyde concentrations were determined by the sodium-sulfite method (Walker, 1964), while methanol concentrations were determined by gas-chromatography. Relative errors are below 2% in both cases. For details, see Hasse (1990).

Table 1. Experimental Results for Vapor–Liquid Equilibria in the System Formaldehyde–Water

T K	p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}
343.1	31.0	0.030	0.029
343.1	30.9	0.064	0.054
343.1	31.2	0.068	0.056
343.1	30.9	0.091	0.071
343.2	30.9	0.110	0.083
343.3	30.7	0.129	0.093
343.1	30.5	0.137	0.098
363.1	71.4	0.051	0.061
363.1	71.4	0.056	0.064
363.2	70.6	0.058	0.066
363.1	71.6	0.150	0.136
383.1	153.1	0.102	0.134
383.3	155.0	0.143	0.169
383.1	155.1	0.253	0.247
383.0	155.1	0.287	0.265
413.2	405.3	0.076	0.155
413.2	414.4	0.106	0.188
413.1	423.1	0.137	0.226
413.2	423.7	0.139	0.221
413.2	432.9	0.171	0.264
413.1	443.1	0.227	0.307
413.1	442.7	0.245	0.334
413.1	449.1	0.304	0.375

Table 2. Experimental Results for Vapor–Liquid Equilibria in the System Water–Methanol

T K	p kPa	$\tilde{x}_{Me}$ mol·mol^{-1}	$\tilde{y}_{Me}$ mol·mol^{-1}
373.1	159.4	0.094	0.423
373.1	166.9	0.114	0.421
373.1	165.3	0.119	0.434
373.1	214.3	0.259	0.604
373.2	228.3	0.329	0.653
373.1	231.8	0.335	0.658
373.1	240.0	0.420	0.767
373.2	279.3	0.588	0.799

To test this apparatus, some data points for vapor–liquid equilibria in the formaldehyde–water binary systems ($T = 343$ and 363 K; $p < 100$ kPa; cf. Table 1), and water–methanol ($T = 373$ K; $p > 100$ kPa; cf. Table 2) were taken. The results agree satisfactorily with data in the literature both for the reacting and the nonreacting systems. Typically, relative deviations are below 2% for partition coefficients and 1% for pressure in both cases. The results in the formaldehyde-water system are shown in Figures 1 and 2.

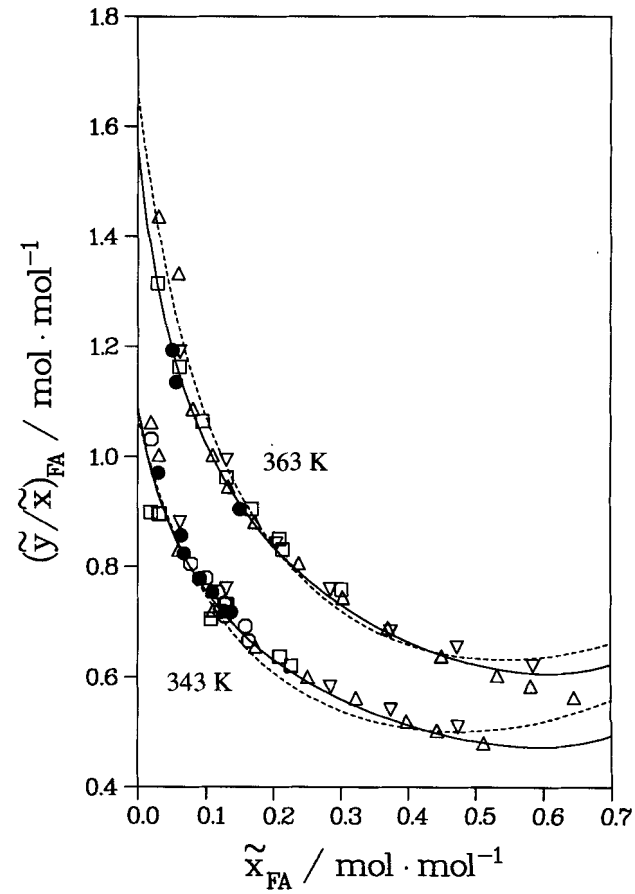

Figure 1. Partition coefficients of formaldehyde in vapor–liquid equilibria in the system formaldehyde–water at 343 and 363 K.

▽ Credali et al. (1965); △ Kogan et al. (1977); □ Maurer (1986); ○ Hasse et al. (1990); ● this work; — — previous model; —— new model.

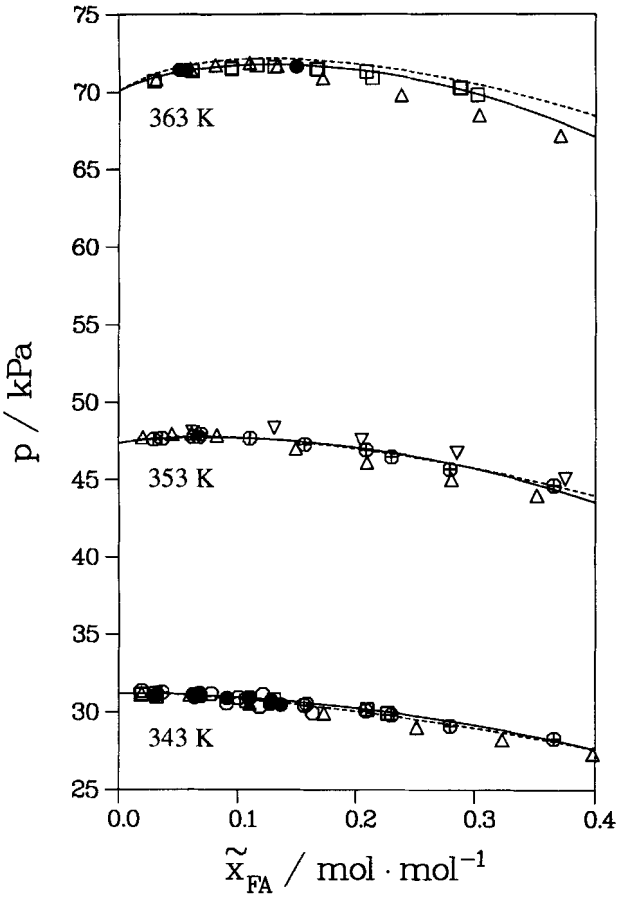

Figure 2. Pressures in vapor–liquid equilibria in the system formaldehyde–water at 343, 353, and 363 K.

▽ Credali et al. (1965); ⊕ Brandani et al. (1976); △ Kogan et al. (1977); □ Maurer (1986); ○ Hasse et al. (1990); ● this work; — — previous model; —— new model.

With the new apparatus vapor–liquid equilibria in the formaldehyde–water system were measured at 383 and 413 K, and pressures were up to 450 kPa. These data will be discussed below. The results of these vapor–liquid equilibrium measurements are reported in Table 1.

Vapor–Liquid Equilibrium Model

The first models for vapor–liquid equilibria in formaldehyde-containing solutions (Kogan, 1979a; Kogan and Ogorodnikov, 1980a,b; and Brandani et al., 1976, 1980) were chemical models, that is, only chemical reactions, but no physical interactions were taken into account. Variations of that type of model continue to appear in the literature (e.g., Masamoto and Matsuzaki, 1994). Maurer (1986) presented a model for vapor–liquid equilibria in formaldehyde-containing systems, in which both chemical reactions and physical interactions between all species were taken into account. That system therefore allows us to consider additional inert components, like trioxane or methylal, in a straightforward manner. This approach has been widely accepted (Brandani et al., 1991a,b, 1992).

The model of Maurer (1986) has continuously been updated and extended as new data became available (Hasse et al., 1990; Hasse and Maurer, 1991a; for a survey, see Hahnenstein et al., 1994a), but the model's structure has not been changed. However, the large amount of new data collected since 1986, especially the recent nuclear magnetic resonance (NMR) spectroscopic studies of Hahnenstein et al. (1994b, 1995), which open the perspective to develop models that explicitly take the kinetic reaction effects into account, have led to the decision to modify the model. The main goals were to improve the model performance at temperatures above 373 K (where new vapor–liquid equilibrium data are now available) and to achieve a better agreement between measured and calculated oligomer distributions in the liquid phase. An accurate description of the oligomer distribution in chemical equilibrium is prerequisite for an extension of the model to include kinetic reaction effects.

As in the original model, the gas phase in the new version is treated as a mixture of ideal gases, and the UNIFAC group contribution method is used to account for physical interactions in the liquid phase. However, the number of UNIFAC groups is reduced in the new model. Furthermore, in the new model, the oligomer distributions in the liquid phase are calculated directly from the overall concentrations, and the equilibrium constants, K_x, which are determined by NMR spectroscopy, are expressed in mole fractions rather than in activities. That thermodynamic inconsistency is the price that has to be paid for the possibility of a straightforward extension of the model to include reaction kinetic effects.

First, we will explain the new model for the binary formaldehyde–water system. The structure of the model for that system is shown in Figure 3. The gas phase is treated as a reacting mixture of ideal gases, containing formaldehyde (FA), water (W), and methylene glycol (MG). Due to the low vapor pressures, no poly(oxymethylene) glycols (MG_i) are present in the gas phase. Hence, physical equilibria have to be considered for formaldehyde, water, and methylene glycol only:

$$p_i^s \cdot x_i \cdot \gamma_i = p_i \qquad i = \mathrm{FA, W, MG}. \tag{1}$$

The activity coefficients of the components of the liquid phase are calculated using the UNIFAC group contribution method (Fredenslund et al., 1975). The total pressure is

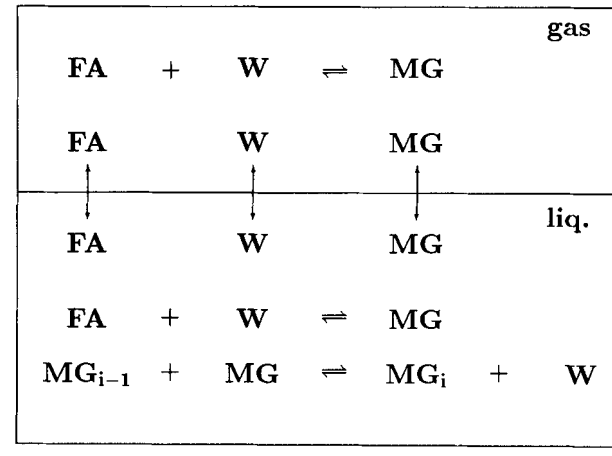

Figure 3. Vapor–liquid equilibrium model for the system formaldehyde–water.

$$p = p_{FA} + p_W + p_{MG}. \quad (2)$$

The true mole fractions in the liquid phase are calculated from overall mole fractions using mass balances and equilibrium constants, K_x, for the liquid-phase reactions (formation of methylene glycol MG and poly(oxymethylene) glycols MG_i):

$$K_{x,MG} = \frac{x_{MG}}{x_{FA} \cdot x_W} \quad (3)$$

$$K_{x,MG_2} = \frac{x_{MG_2} \cdot x_W}{x_{MG} \cdot x_{MG}} \quad (4)$$

$$K_{x,MG_i} = \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}} \quad \text{for all } i > 2 \quad (5)$$

$$\tilde{x}_{FA} = s \cdot \left(x_{FA} + x_{MG} + \sum_{i=2}^{\infty} i \cdot x_{MG_i} \right) \quad (6)$$

$$\tilde{x}_W = s \cdot \left(x_W + x_{MG} + \sum_{i=2}^{\infty} x_{MG_i} \right) \quad (7)$$

$$s = \left(1 + x_{MG} + \sum_{i=2}^{\infty} i \cdot x_{MG_i} \right)^{-1}. \quad (8)$$

As indicated by Eqs. 4 and 5, Hahnenstein et al. (1994b) distinguish between K_{x,MG_2} (formation of MG_2) and K_{x,MG_i}, $i > 2$ (formation of all higher poly(oxymethylene) glycols). The equilibrium constant $K_{x,MG}$ for the formation of methylene glycol in the liquid phase (for which only inconsistent spectroscopic information is available) is calculated from the equilibrium constant K for the same reaction in the gas phase (which is known from densimetric studies, Kogan, 1979b):

$$K_{x,MG} = K_{MG} \cdot \frac{p^s_{FA} \cdot p^s_W}{p^s_{MG} \cdot p^\theta} \cdot \frac{\gamma_{FA} \cdot \gamma_W}{\gamma_{MG}}. \quad (9)$$

For a discussion of the algorithm used to solve these equilibrium conditions, see Hasse (1990).

In many cases, it is possible to completely neglect the small amounts of monomeric formaldehyde in the liquid phase. This leads to an important simplification of the numerical solution of the equilibrium conditions. Furthermore, when overall formaldehyde concentrations are low—for example, in most environmental problems—formaldehyde is almost exclusively bound in methylene glycol, and the equations can be simplified further, so that they can be solved analytically. More details are given in the Appendix.

The model for the formaldehyde–water system is easily adapted to describe the formaldehyde–methanol system. The calculation of the true liquid-phase concentration is somewhat simpler in that system than in formaldehyde–water, as no distinction between the equilibrium constants of the formation of different poly(oxymethylene) hemiformals is required (only one K_{x,HF_i} for all $i > 1$; see Hahnenstein et al., 1994b). The model for the ternary formaldehyde–water–methanol system is a superposition of the models for the binary subsystems.

Table 3. Chemical Equilibrium Constants*

Reaction	A_1	B_1
K_{MG}	-1.698×10^1	$+5.233 \times 10^3$
K_{HF}	-1.627×10^1	$+6.462 \times 10^3$
K_{x,MG_2}	$+1.449 \times 10^{-2}$	$+5.609 \times 10^2$
K_{x,MG_i}, $i > 2$	-1.084×10^{-1}	$+4.604 \times 10^2$
K_{x,HF_i}, $i > 1$	-3.476×10^{-1}	-5.032×10^2

*$\ln K = A_1 + \frac{B_1}{T/K}$.

Vapor pressures, chemical equilibrium constants, and UNIFAC parameters are needed for calculating vapor–liquid equilibria. The equilibrium constants of gas-phase reactions I and III were taken directly from densimetric studies (Kogan, 1979b), and the equilibrium constants of the formaldehyde oligomer-formation reactions II and IV in the liquid phase were taken from recent NMR spectroscopic studies (Hahnenstein et al., 1994b). Therefore, the true concentrations in both phases calculated with the model are in agreement with experimental data. Also the estimates for the true concentration of monomeric formaldehyde in the liquid phase are in acceptable agreement with the widely scattered spectroscopic results (for references, see Hasse and Maurer, 1991b). The chemical equilibrium constants used in the model are given in Table 3.

Since neither methylene glycol nor hemiformal exists as pure substances, their vapor-pressure curves were determined from vapor–liquid equilibrium data for the binary formalde-hyde–water and formaldehyde–methanol systems, respectively. The Antoine equation was used to describe the vapor pressures (Table 4). Figure 4 shows a comparison of the vapor-pressure curve of methylene glycol with vapor-pressure curves of hydrogen peroxide and other diols. It can be seen that the methylene glycol vapor-pressure curve determined in the present work is reasonable. The good agreement of the slopes of the different vapor-pressure curves shown in Figure 4 indicates, that the new vapor-pressure curve of methylene glycol also gives a reasonable estimate for the enthalpy of vaporization.

As shown in Table 5, the number of UNIFAC groups in the new model is reduced from eight (in the previous model version) to five. The method of dividing components into UNIFAC groups is now completely analogous, both for the formaldehyde–water and the formaldehyde–methanol systems. The UNIFAC size and surface parameters are given in Table 6, and the UNIFAC interaction parameters are given in Table 7.

Some of the interaction parameters had to be fitted, since using groups and parameters from UNIFAC parameter ta-

Table 4. Vapor Pressures*

Substance	A_2	B_2	C_2
Formaldehyde	14.4625	−2,204.13	−30.15
Water	16.2886	−3,816.44	−46.13
Methylene glycol	18.3287	−5,699.81	−2.20
Methanol	16.5725	−3,626.55	−34.29
Hemiformal	19.5344	−5,637.26	0

*$\ln \frac{p^s}{\text{kPa}} = A_2 + \frac{B_2}{T/K + C_2}$.

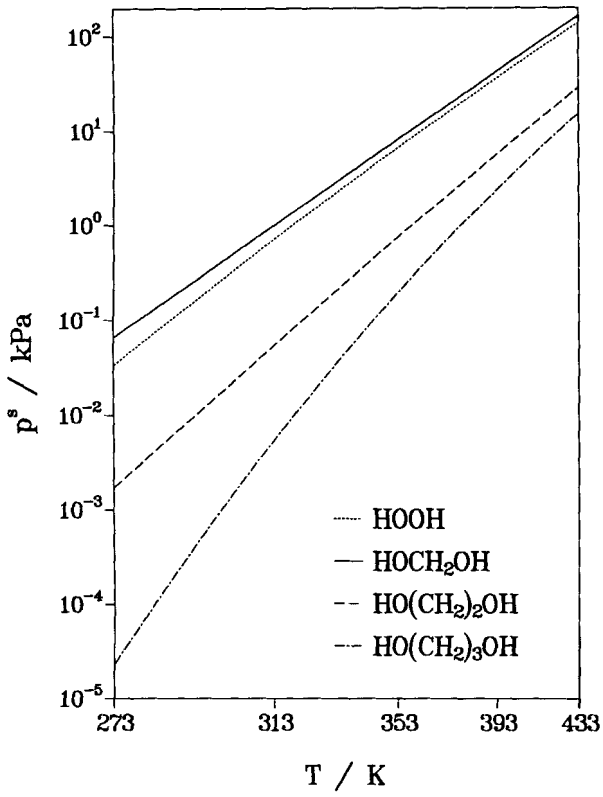

Figure 4. Vapor pressure of methylene glycol $HOCH_2OH$ determined in this work vs. vapor pressures of hydrogen peroxide (D'Ans Lax, 1967) and some other diols (Reid et al., 1977).

bles (Hansen et al., 1991) did not yield satisfactory results. Only parameters for interactions, where one partner is either methylene glycol or hemiformal (which cannot be obtained as pure substances), were fitted to binary vapor–liquid equilibrium data of formaldehyde-containing systems (formaldehyde–water: interactions between water (W) and methylene glycol (MG); formaldehyde–methanol: interactions between methanol (Me) and hemiformal (HF)). Furthermore, one pair of UNIFAC parameters was fitted to ternary data for the formaldehyde–water–methanol system (interactions between water (W) and hemiformal (HF) groups, which do not occur in binary systems).

Parameters for interactions between water (W) and methanol (Me) were determined in the present work from experimental data on vapor–liquid equilibria in the binary water–methanol system at temperatures between 298 and 423

Table 5. Division of Components of Aqueous and Methanolic Formaldehyde Solutions into UNIFAC Groups

Component	Groups
CH_2O	1 FA
H_2O	1 W
$HOCH_2OH$	1 MG
$HO(CH_2O)_iH$	i FA, 1 W, $i>1$
CH_3OH	1 Me
$HOCH_2OCH_3$	1 HF
$HO(CH_2O)_iCH_3$	i FA, 1 Me, $i>1$

Table 6. UNIFAC Size and Surface Parameters

Group	r	q
CH_2O	0.9183	0.780
H_2O	0.9200	1.400
$HO(CH_2O)H$	2.6744	2.940
CH_3OH	1.4311	1.432
$HO(CH_2O)CH_3$	2.3494	2.212

K (Table 7). Using these parameters leads to a slightly better correlation of the data referred to in Table 7 than using the parameters of Hansen et al. (1991). All other UNIFAC parameters were preset using assumptions or analogies.

Comparison with Vapor–Liquid Equilibrium Data

In Figures 1, 2 and 5–10, experimental data for vapor–liquid equilibria are compared to the results obtained with the new model version. Formaldehyde partition coefficients in the formaldehyde–water system are described accurately in the whole temperature range. In most cases, relative deviations between calculations and experimental results are below 5%. Calculated pressures generally agree with the experimental results within 2% (Figure 2). Figure 5 shows that the results from the new model agree well both with the experimental results of Olsson and Svensson (1975) at 393 K and with new data from the present work at 413 K. This proves that both data sets are consistent. Differences between the old and the new model are rather small as long as the temperature is between 323 and 373 K. At higher temperatures, however, the new model yields a distinctly improved agreement with the experimental data (Figure 5). But also at lower temperatures the new model gives improvements over the previous version, especially at low and high formaldehyde concentrations (Figure 6).

Typical results of the comparison of calculations with experimental data for the formaldehyde–methanol system are shown in Figure 7 (partition coefficients of formaldehyde) and Figure 8 (pressures). Again, relative deviations between the experimental data and the calculation are generally below 5% for partition coefficients and 2% for pressure. The differ-

Table 7. UNIFAC Interaction Parameters

i \ j	FA	W	MG	Me	HF
FA	0.00	240.00*	0.00†	339.70*	0.00†
W	−149.00*	0.00	497.27‡	293.66§	18.11#
MG	0.00†	−354.97‡	0.00	293.66**	0.00†
ME	−180.60*	−194.10§	−194.10**	0.00	−41.70††
HF	0.00†	14.03#	0.00†	58.36††	0.00

*From Maurer (1986).
†Neglected.
‡Fitted to VLE data for the system formaldehyde-water: this work; Hasse and Maurer (1991a); Hasse et al. (1990); Maurer (1986); Kogan et al. (1977); Olsson and Svensson (1975).
§Fitted to VLE data for the system water–methanol: taken from Gmehling and Onken (1977): Butler et al.; Dalager; Dulitskaya; Green and Venner; Kohoutova et al.; McGlashan and Williamsson; Olevsky and Golubev; Othmer and Benenati; Ratcliff and Chao; Reamer et al.; taken from Gmehling et al. (1981): Hall et al.; Hirata and Suda; Swami et al.
#Fitted to VLE data for the system formaldehyde–water–methanol: Hasse and Maurer (1991a); Maurer (1986); Kogan and Ogorodnikov (1980b).
**Analogy: $a_{MG,Me} = a_{W,Me}$; $a_{Me,MG} = a_{Me,W}$.
††Fitted to VLE data for the system formaldehyde-methanol: Hasse and Maurer (1991a); Kogan and Ogorodnikov (1980a).

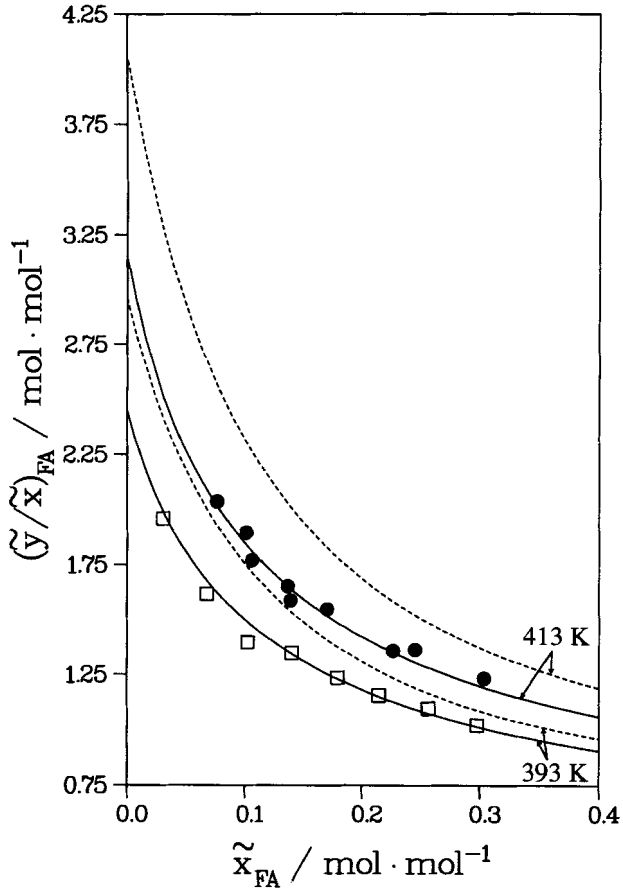

Figure 5. Partition coefficients of formaldehyde in vapor–liquid equilibria in the system formaldehyde–water at 393 and 413 K.

□ Olsson and Svensson (1975); ● this work; — — previous model; —— new model.

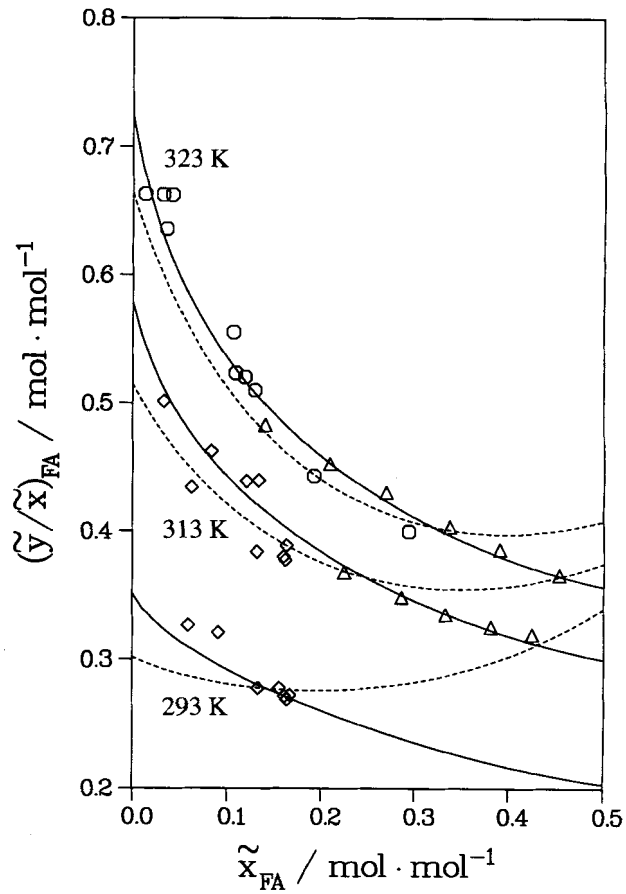

Figure 6. Partition coefficients of formaldehyde in vapor–liquid equilibria in the system formaldehyde–water at 293–323 K.

△ Kogan et al. (1977); ○ Hasse et al. (1990); ◇ Hasse and Maurer (1991a); — — previous model; —— new model.

ences between the previous and the new model version are smaller than in the formaldehyde–water system, but again the new model gives the better agreement with experimental results.

Also in the ternary formaldehyde–water–methanol system, the model gives a reliable description of the experimental data (relative deviations generally below 10% for partition coefficients and 3% for the pressure). Some typical examples are shown in Figures 9 and 10.

In previous work, a strong influence of the addition of small amounts of methanol on the partition coefficient of formaldehyde in vapor–liquid equilibria of aqueous formaldehyde solutions was observed (Hasse and Maurer, 1991a). This effect was only qualitatively (but not quantitatively) predicted by the previous version of the model. Despite careful consideration of different possibilities of developing the model, the quantitative description could not be essentially improved in that area. Further efforts to improve the model only seem to be reasonable if more data on vapor–liquid equilibria in the formaldehyde–water–methanol system are available at small methanol concentrations.

Enthalpy Model

Liu et al. (1992) described an enthalpy model for aqueous and methanolic formaldehyde solutions. That model was modified in the present work. The way the temperature dependence of the enthalpy of vaporization of pure components is treated is simplified, though not essentially changed. The excess enthalpies in the liquid phase are completely neglected, as they are so small that they do not significantly affect enthalpy changes upon vaporization (Hasse and Maurer, 1992). Furthermore, for the calculation of the true concentrations in the liquid and the gas phase, the procedure used in the new version of the vapor–liquid equilibrium model is applied.

The basic equations are only briefly reported here: The enthalpies of pure gaseous formaldehyde, water, and methanol at $T^\theta = 273.15$ K are set to zero:

$$h_i^g(T^\theta) = 0, \qquad i = \text{FA, W, Me.} \tag{10}$$

At other temperatures, the enthalpies of these components in the gas phase are calculated using ideal gas heat capacities:

$$h_i^g(T) = \int_{T^\theta}^{T} c_{p,i}(T)\, dT, \qquad i = \text{FA, W, Me.} \tag{11}$$

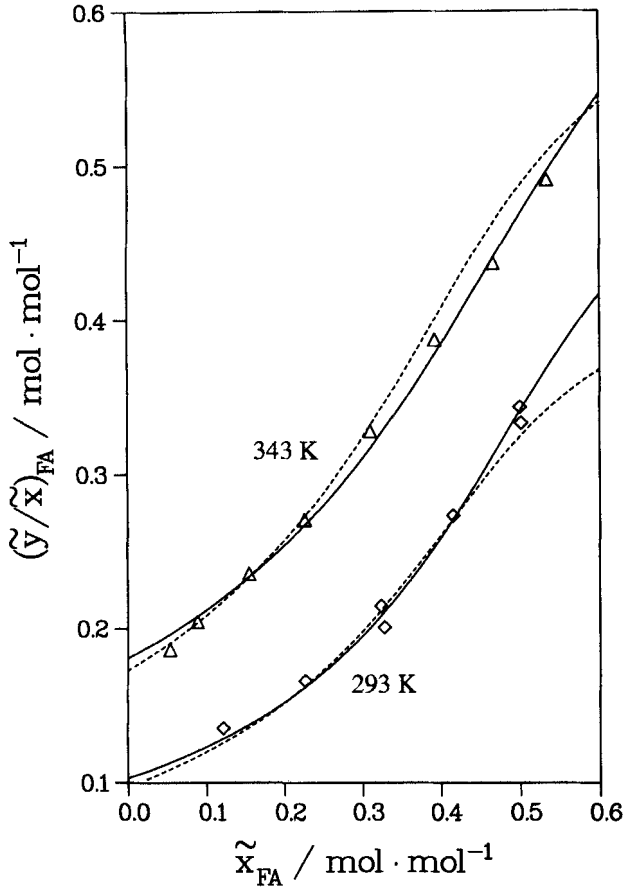

Figure 7. Partition coefficients of formaldehyde in vapor–liquid equilibria in the system formaldehyde–methanol at 293 and 343 K.

△ Kogan and Ogorodnikov (1980a); ◇ Hasse and Maurer (1991a); — — previous model; —— new model.

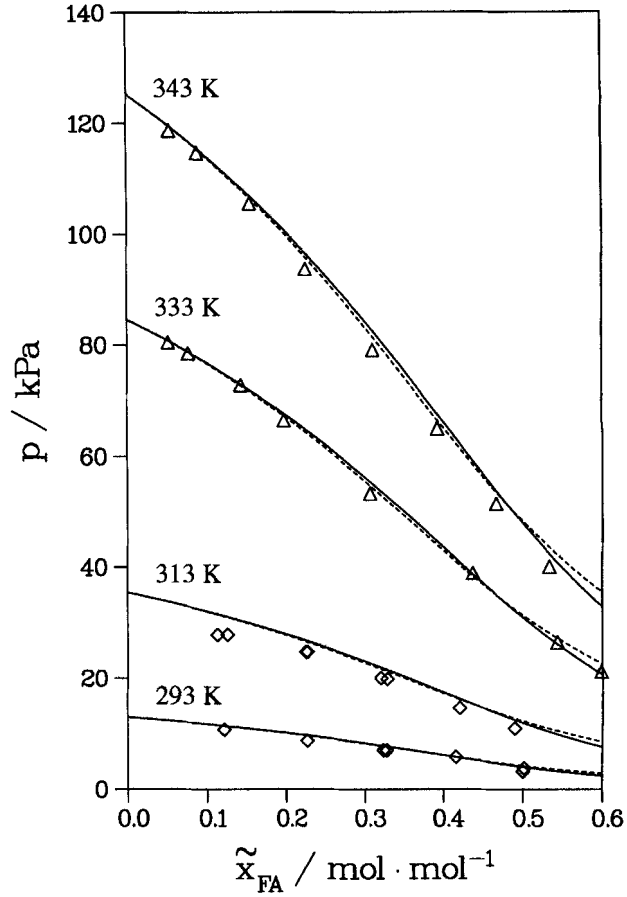

Figure 8. Pressures in vapor–liquid equilibria in the system formaldehyde–methanol at 293–343 K.

△ Kogan and Ogorodnikov (1980a); ◇ Hasse and Maurer (1991a); — — previous model; —— new model.

The enthalpies of methylene glycol and hemiformal in the gas phase are calculated from reaction enthalpies:

$$h^g_{MG}(T) = h^g_{FA}(T) + h^g_W(T) + \Delta_R h^g_{MG}(T) \qquad (12)$$

$$h^g_{HF}(T) = h^g_{FA}(T) + h^g_{Me}(T) + \Delta_R h^g_{HF}(T). \qquad (13)$$

The enthalpies of the pure components formaldehyde, water, methanol, methylene glycol, and hemiformal in the liquid phase are calculated from the enthalpies of these components in the gas phase and enthalpies of vaporization:

$$h^l_i(T) = h^g_i(T) - \Delta h_{V,i}(T), \qquad i = \mathrm{FA, W, Me, MG, HF}. \qquad (14)$$

The enthalpies of the formaldehyde oligomers in the liquid phase result from:

$$h^l_{MG_i}(T) = h^l_{MG_{i-1}}(T) + h^l_{MG}(T) - h^l_W(T) + \Delta_R h_{MG_i}(T), \qquad i > 1 \quad (15)$$

$$h^l_{HF_i}(T) = h^l_{HF_{i-1}}(T) + h^l_{HF}(T) - h^l_{Me}(T) + \Delta_R h_{HF_i}(T), \qquad i > 1. \quad (16)$$

The molar enthalpies of liquid and gaseous mixtures are found from:

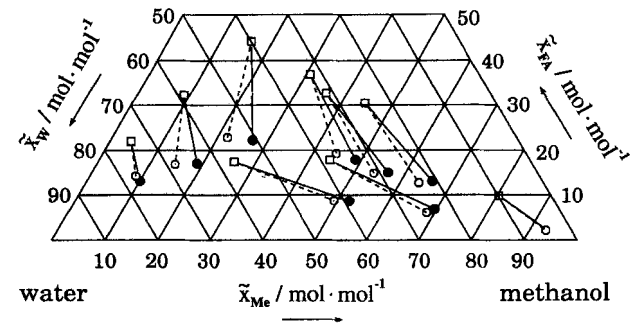

Figure 9. Concentrations in vapor–liquid equilibria in the system formaldehyde–water–methanol at 343 K (pressures between 32 and 104 kPa).

□ Liquid phase; ○ gas phase (exp., Maurer, 1986); ● gas phase (calc., new model).

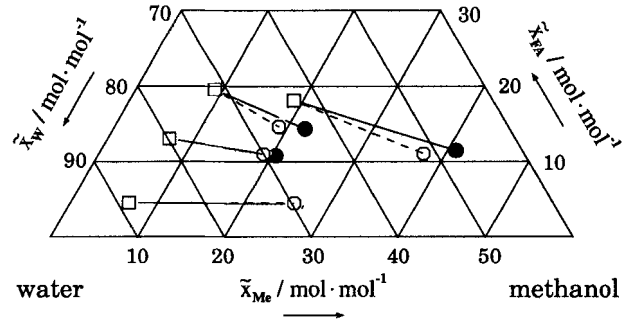

Figure 10. Concentrations in vapor–liquid equilibria in the system formaldehyde–water–methanol at 363 K (pressures between 85 and 102 kPa).

□ Liquid phase; ○ gas phase (exp., Maurer, 1986); ● gas phase (calc., new model).

$$h^l(T) = \sum_{\text{all } i} x_i \cdot h_i^l(T) \tag{17}$$

$$h^g(T) = \sum_{\text{all } i} y_i \cdot h_i^g(T). \tag{18}$$

The true concentrations in the liquid and the gas phases x_i and y_i are calculated as in the vapor–liquid equilibrium model from overall concentrations and chemical equilibrium constants. Overall molar enthalpies are determined using the mass balances (for details, see Hasse, 1990).

Enthalpies of vaporization of the pure components can be calculated from their vapor-pressure curves, and reaction enthalpies can be found from the chemical equilibrium constants (Tables 3 and 4):

$$\Delta h_V(T) = -\frac{R \cdot B_2}{\left(1 + \frac{C_2}{T/K}\right)^2} \tag{19}$$

$$\Delta_R h(T) = -R \cdot B_1. \tag{20}$$

Therefore, beside information already used in the vapor–liquid equilibrium model, only the ideal gas heat capacities of formaldehyde, water, and methanol have to be known. The data for formaldehyde were taken from Liu et al. (1992), and the data for methanol from Reid et al. (1987). The ideal gas heat capacity of water was fitted to enthalpy data of pure water in the gas phase (Schmidt, 1982). These parameters are given in Table 8.

Enthalpy changes upon isothermal vaporization do not depend on these heat capacities. So, these enthalpy changes are completely predicted from the information already used in the vapor–liquid equilibrium model.

Table 8. Ideal Gas Molar Heat Capacities c_p of Pure Components*

	A_3	B_3	C_3	D_3
FA	3.314×10^{1}	-1.183×10^{-2}	6.653×10^{-5}	÷
W	3.900×10^{1}	-1.131×10^{-1}	6.434×10^{-4}	-1.122×10^{-6}
Me	2.115×10^{1}	-7.092×10^{-2}	2.588×10^{-5}	-2.852×10^{-8}

*c_p/(J · mol^{-1} · K^{-1}) = $A_3 + B_3(T/K) + C_3(T/K)^2 + D_3(T/K)^3$.

Table 9. Enthalpies of Vaporization*

Substance	T_c K	T_1 K	$\Delta h_V(T_1)$ kJ · mol^{-1}	n^W
W	647.30	373.15	40.661	0.33714
Me	512.60	337.85	35.279	0.35375

*Δh_V/(kJ · mol^{-1}) = $\Delta h_V(T_1)\left(\frac{1-T_r}{1-T_{r1}}\right)^{n^W}$.

Table 10. Improved Parameters of the Enthalpy Model*

z	A_z	B_z
$\Delta h_{V,\text{HF}}$	36.668	0.0
$\Delta_R h_{\text{MG}}$	−29.978	−86.50

*z/(kJ · mol^{-1}) = $\frac{A_4}{\left(1+\frac{B_4}{T/K}\right)^2}$, $z = \Delta h_V$, or $\Delta_R h$.

Comparison with Calorimetric Data

Results of calculations can be compared to experimental data for enthalpy changes upon partial vaporization of formaldehyde-containing mixtures (Liu et al., 1992). Equations 19 and 20 were used together with the data on vapor pressures and chemical equilibrium constants given in Tables 3 and 4 to predict the experimental results of Liu et al. (1992).

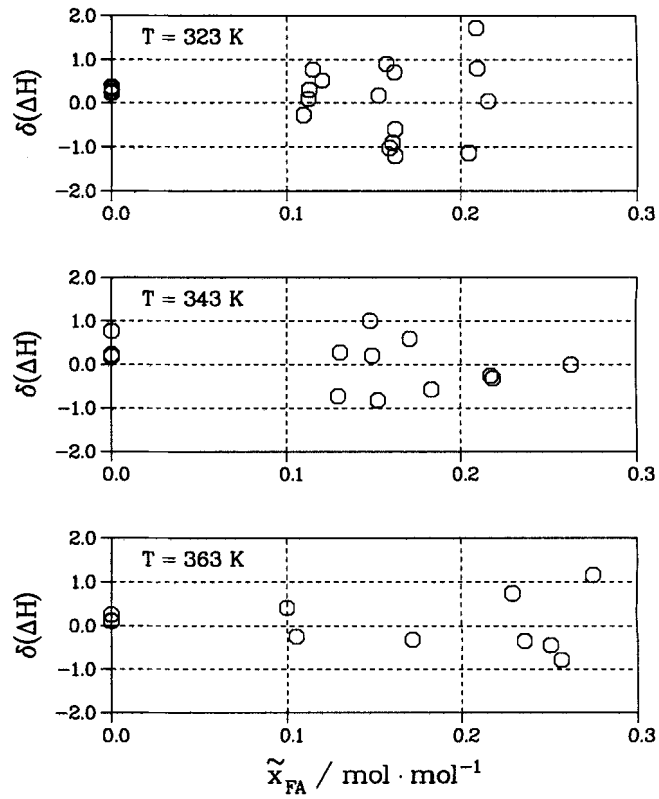

Figure 11. Measured vs. calculated enthalpy changes on partial vaporization of aqueous formaldehyde solutions as a function of the overall formaldehyde concentration in the liquid phase at the calorimeter outlet.

○ Liu et al. (1992).

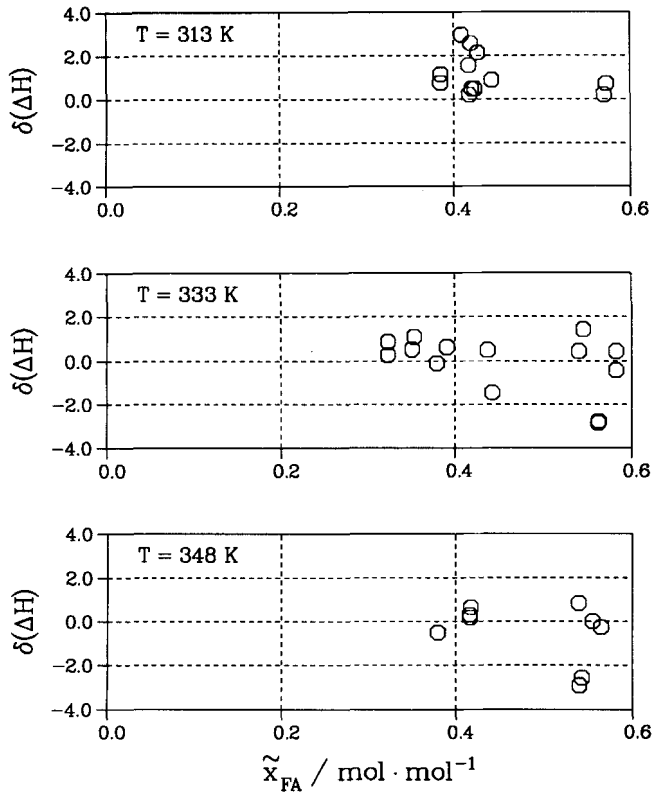

Figure 12. Comparison between measured and calculated enthalpy changes upon partial vaporization of formaldehyde solutions in methanol and water ($\tilde{x}_W < 0.04$ mol · mol^{-1}) as a function of the overall formaldehyde concentration in the liquid phase at the calorimeter outlet.

○ Liu et al. (1992).

Relative deviations between predicted and measured enthalpy changes were mostly below 5% for the formaldehyde–water system, and between 5 and 10% for the formaldehyde–methanol system.

If more accurate enthalpy calculations are needed, the enthalpies of vaporization of pure water and methanol can be calculated with the Watson equation:

$$\Delta h_V(T) = \Delta h_V(T_1)\left(\frac{1-T_r}{1-T_{r1}}\right)^{n^W} \tag{21}$$

where $\Delta h_V(T_1)$ is the enthalpy of vaporization at the reduced temperature $T_r = T_1/T_c$. The parameters needed to calculate the enthalpies of vaporization of water and methanol are given in Table 9. The exponents n^W were fitted to more accurate experimental data (water: Schmidt, 1982; methanol: *VDI-Wärmeatlas*, 1994; Svoboda et al., 1973; and Fiock et al., 1931). Relative errors are typically below 0.5% for water and 1% for methanol. Furthermore, the data for the enthalpy of vaporization of hemiformal and for the reaction enthalpy of the methylene glycol formation in the gas phase, was fitted to the calorimetric data of the formaldehyde solutions of Liu et al. (1992). These parameters are given in Table 9 (the adjusted parameters are the same as those already used by Liu et al., 1992). The enthalpy model with the parameters from Tables 9 and 10 correlates the experimental data of Liu et al. (1992) with relative deviations, mostly below 2%, as can be seen from Figures 11 and 12.

Conclusion

In this work, the physicochemical model for vapor–liquid equilibria in the formaldehyde-containing mixtures of Maurer (1986) was revised on the basis of new experimental data for chemical equilibria as well as for vapor–liquid equilibria. In the new model, NMR data on chemical equilibria are used, so that the true concentrations calculated with the model are in agreement with spectroscopic data, and the equilibrium model can be extended directly to a kinetic model on the basis of new spectroscopic and densimetric kinetic reaction data.

With a vapor–liquid equilibrium apparatus, which was especially constructed for this purpose, new data on vapor–liquid equilibria in the formaldehyde–water system were taken at temperatures up to 413 K. These data extend the temperature range, where reliable information on vapor–liquid equilibria is available. Over that range (293–413 K), the new model correlates well vapor–liquid equilibrium data of aqueous and methanolic formaldehyde-containing solutions (partition coefficients within 5%; pressures within 2% in most cases).

Without any modification, the extension of the vapor–liquid equilibrium model to enthalpy changes upon vaporization of formaldehyde-containing mixtures gives predictions that agree with the experimental data within about 5%. By adjusting some of the model parameters to calorimetric data, the deviations are reduced to below 2%.

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Notation

A = adjustable parameter
a = UNIFAC interaction parameter
B = adjustable parameter
C = adjustable parameter
c_p = ideal gas molar heat capacity
D = adjustable parameter
H = enthalpy
h = molar enthalpy
i = number of CH_2O groups in formaldehyde reaction products
$\bar{i}$ = average number of CH_2O groups in formaldehyde reaction products
liq = liquid
p_i = partial pressure of component i
p^s = vapor pressure
p^θ = standard pressure (101.325 kPa)
q = UNIFAC-surface parameter
R = universal gas constant
r = UNIFAC-size parameter
s = abbreviation (cf. Eq. 8)
T = absolute temperature
T^θ = reference temperature (273.15 K)
$T_r = T/T_c$
x = true mole fraction in liquid phase

$\tilde{x}$ = overall mole fraction in liquid phase
y = true mole fraction in gas phase
$\tilde{y}$ = overall mole fraction in gas phase
z = abbreviation

Greek letters

γ = activity coefficient
γ^{∞} = limiting activity coefficient
$\delta(\Delta H) = 100(\Delta H_{calc} - \Delta H_{exp})/\Delta H_{exp}$
Δh_V = enthalpy of vaporization
$\Delta_R h$ = reaction enthalpy

Subscripts

c = critical point
calc = calculated
exp = experimental
j = group
max = maximal
1, 2, 3, 4 = different correlations

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Appendix: Simplified Model

In many cases of practical interest, it is possible to use a simplified version of the model, allowing a faster solution of the equilibrium conditions. Two simplifications are discussed here using the formaldehyde–water system as an example,

but the methods can be applied for the formaldehyde–methanol system as well.

It is only because of the concentration dependence of the activity coefficients in the expression for the equilibrium constant of the methylene glycol formation in the liquid phase (Eq. 9) that an iterative procedure is needed to solve the equilibrium conditions (Eqs. 1–9). However, in many cases the small amounts of monomeric formaldehyde in the liquid phase can be neglected and, hence, that iteration can be avoided (Eq. 9 is then not needed). In that case, the partial pressure of monomeric formaldehyde in the gas phase is obtained from

$$p_{FA} = \frac{1}{K_{MG}} \cdot \frac{p_{MG} \cdot p^{\theta}}{p_{A,W}}. \tag{A1}$$

Despite the simplifying assumption, it is still possible to estimate the amount of monomeric formaldehyde in the liquid phase from

$$x_{FA} = \frac{p_{FA}}{p^{s}_{FA} \cdot \gamma^{\infty}_{FA}} \tag{A2}$$

using the activity coefficient of formaldehyde at infinite dilution γ^{∞}_{FA} determined from the UNIFAC model.

For aqueous solutions with low overall formaldehyde concentrations (those of importance in many environmental problems), it is possible to further simplify the model: At overall formaldehyde concentrations below about 0.01 mol·mol^{-1} and temperatures below about 373 K, formaldehyde is almost exclusively bound in methylene glycol. So both monomeric formaldehyde and the poly(oxymethylene) glycols can be neglected (such solutions only contain water and methylene glycol). The mass balance then yields

$$x_{MG} = \frac{\tilde{x}_{FA}}{1 - \tilde{x}_{FA}} \tag{A3}$$

$$x_{W} = 1 - x_{MG}. \tag{A4}$$

The activity coefficients of water and methylene glycol can then be calculated from the overall composition, and Raoult's law (Eq. 1) yields the partial pressures of these substances in the gas phase. The partial pressure of formaldehyde, which must not be neglected, is found from Eq. A1. The overall concentration of formaldehyde in the gas phase is

$$\tilde{y}_{FA} = \frac{p_{FA} + p_{MG}}{p + p_{MG}}, \tag{A5}$$

where p is the total pressure according to Eq. 2.

From Eqs. A3–A5 an analytical expression for the overall partition coefficient of formaldehyde $(\tilde{y}/\tilde{x})_{FA}$ at low formaldehyde concentrations can be found:

$$\lim_{\tilde{x}_{FA} \to 0} \left(\frac{\tilde{y}}{\tilde{x}}\right)_{FA} = \frac{p^{s}_{MG}}{p^{s}_{W}} \cdot \gamma^{\infty}_{MG,W} \left(1 + \frac{p^{\theta}}{p^{s}_{W} \cdot K_{MG}}\right). \tag{A6}$$

That result for the limiting overall partition coefficient, which was derived here from the simplified model, is identical with that obtained from the full model.

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