Vapor-Liquid Equilibrium of Formaldehyde- and Water-Containing Multicomponent Mixtures

The vapor-liquid equilibria in the binary mixtures water-formaldehyde and methanol-formaldehyde are precisely correlated by introducing a physicochemical model that takes into account physical forces of interactions as well as chemical reactions. The most valuable feature of the model is its simple extension to multicomponent mixtures. From binary data alone the model is capable of accurately predicting vapor-liquid equilibria in complex mixtures such as formaldehyde-water-trioxane and formaldehyde-water-methanol. This is demonstrated by comparing calculated data with experimental results taken from the literature or measured in this work, at temperatures between about 310 and 400 K at pressures up to 500 kPa, and formaldehyde concentrations in the liquid phase of up to about 70 mol %.

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Formaldehyde is an important raw material for the preparation of many products of the chemical industry—for example, plastics and adhesives—and is produced on a large scale. Because of its extremely high reactivity, formaldehyde is almost never prepared in the pure form, but is usually produced, stored, and processed further in the form of aqueous solutions.

The marked tendency for reaction with other substances is a sizable obstacle to modeling the vapor-liquid phase equilibrium in multicomponent aqueous formaldehyde solutions. While several methods to correlate the vapor-liquid phase equilibrium of the binary system formaldehyde-water have been described in the literature (Walker, 1964; Brandani et al., 1980; Kogan et al., 1977), there is virtually no method for modeling the vapor-liquid equilibrium in water- and formaldehyde-containing multicomponent mixtures with sufficient accuracy. The study presented here therefore refers to the development and testing of such a method. At first the binary system formaldehyde-water is considered, then the method is extended to ternary systems, the third component being either chemically inert—e.g., trioxane—or chemically reactive with formaldehyde as methanol.

CONCLUSIONS AND SIGNIFICANCE

Despite the appreciable industrial importance of substances in addition to formaldehyde and water that react with each other and contain inert or reactive components, there is no reliable method available in the literature for describing the vapor-liquid equilibrium in such a mixture. Therefore a model was developed that, by taking into account intermolecular forces between the various types of molecules in the liquid phase as well as the most important chemical reactions, accurately predicts from information on binary systems alone, the vapor-liquid equilibrium in multicomponent formaldehyde and water-containing mixtures.

The correlation starts from a model for the binary

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system formaldehyde-water. The equilibrium constants for the most important chemical reactions—e.g., the formation of methylene glycol and polyoxymethylenes—are determined from density data for the gaseous phase and nuclear magnetic resonance spectra for the liquid phase. Intermolecular interactions are described by the UNIFAC method; interaction parameters are taken from the literature or estimated. Only one quantity had to be fitted to some experimental vapor-liquid equilibrium (VLE) data: the vapor pressure of methylene glycol—the simplest combination of water and formaldehyde, but one that cannot be prepared in pure form.

The model accurately represents measurements in the entire investigated range of state, e.g., at temperatures between about 300 and 400 K under pressures between about 5 and 250 kPa, corresponding to formaldehyde concentrations of up to about 70 wt. % in the liquid phase.

As formaldehyde reacts with methanol very much as it does with water, the model is easily adopted to the binary system formaldehyde-methanol. As examples for extensions to multicomponent formaldehyde- and water-containing mixtures, the ternary mixtures of formaldehyde with water and trioxane and of formaldehyde with water and methanol are considered, demonstrating—starting from information on binary systems alone—that the model is able to accurately predict VLE data also when more chemically inert as well as chemically reactive components are present.

For these mixtures at temperatures between about 330 and 370 K and formaldehyde concentrations up to about 70 mol % in the liquid phase, the standard deviation between predicted and measured data for the total pressure as well as for the concentrations in the vapor phase is about 3 to 7%.

As literature data on VLE of formaldehyde-containing mixtures usually scatter considerably, new experimental data had to be determined for the binary system with water and on both ternary systems. These new experimental results are also reported and included in the comparison.

Introduction

The thermodynamics of the vapor-liquid phase equilibrium are a key factor in the design of distillation processes. The phase equilibrium condition is customarily written as an equation linking the fugacities of a component in the two phases. In most applications in the chemical industry it is necessary to base the calculation of the fugacity for the two phases on different reference states. The deviations from the reference states are expressed through dilution and correction terms. There are two different methods for describing the correction terms, i.e., the fugacity or activity coefficients. In the physical method it is assumed that the corrections need to be introduced because the physical forces of interaction that are experienced by a component in the mixture differ from those in the reference state. In the chemical method, by contrast, it is assumed that correction terms are caused by chemical reactions due to which the true mole fractions differ from the overall or stoichiometric mole fractions.

Physical methods, such as the WILSON, NTRL, UNIQUAC, ASOG, and UNIFAC models for describing the activity coefficients in the liquid phase, and the two-coefficient truncated virial equation for describing the fugacity coefficients in the gaseous phase, have become standard tools in calculations of thermodynamic phase equilibria. This is chiefly because assuming the forces of interaction to be additive and restricting the interactions to those between pairs of particles, usually provides a fairly good description of the true situation in fluid mixtures, which is why the physical theories can be simply extended from binary to multicomponent mixtures. By contrast, it is rare for the transfer of results from chemical models for binary systems to multicomponent systems to be successful, an instance of such a successful transfer being the dimerization of organic acids in the gas phase. Yet even the purely physical methods frequently do not provide sufficiently accurate descriptions of the concentration dependence of the activity coefficients, in particular whenever the interactions in the mixtures between the various types of molecule are highly nonuniform and it is likely for association effects bordering on chemical reactions to be present. For that reason, the purely physical theories have been increasingly broadened in recent years by the introduction of a "chemical" correction term, as for example in the work of Neau and Peneloux (1979), Nagata (1977), Brandani and Prausnitz (1981), and Nath and Bender (1981). This introduction is usually done formally by supplementing the two binary parameters contained in the physical theories with a further, third parameter, thereby making the models more flexible. However, the improvements are still not sufficient in cases where chemical reactions in the mixture give rise to genuinely new types of particles that do not occur in pure form.

The group of industrially important mixtures whose vapor-liquid phase equilibrium has to date been described by means of chemical theories includes the mixture of water and formaldehyde. Examples of work that may be mentioned in this context are the papers by Kogan (1979a,b,c) and Brandani et al. (1980). However, these purely chemical models can hardly be extended in a straightforward manner to multicomponent systems, such as aqueous formaldehyde solutions that additionally contain substances such as methanol, butynediol, glyoxal, trioxane, formic acid, or dichloroethane. Consequently, there is no reliable method available for modeling the vapor-liquid equilibrium (VLE) of these multicomponent mixtures, which frequently occur in the chemical industry. These mixtures are known to give rise to chemical reactions, not only in the liquid but also in the gas phase, that lead to substances which are virtually impossible to prepare in the pure form. Furthermore there are appreciable differences in the physical forces of interaction between the various molecules in these mixtures. The phase equilibrium in these mixtures is logically best described, therefore, with a model that takes into account both chemical reactions and physical forces of interaction.

Modeling of the Vapor-Liquid Equilibrium for the Binary System Formaldehyde-Water

The starting point for any model of the vapor-liquid equilibrium of aqueous formaldehyde-containing multicomponent mixtures must be the description of the binary system formaldehyde-water. It has long been known (e.g., Walker, 1964, p. 140) that formaldehyde reacts with water. Figure 1 shows the most important reactions. If one tries to concentrate aqueous formaldehyde solutions by evaporation, solid paraformaldehyde (also known as polyoxymethylene) precipitates from the liquid solution. Polyoxymethylene is a polymer of a large number of formaldehyde molecules, which can gradually grow from the simplest reaction product between formaldehyde and water, namely methylene glycol. In acid or alkaline solution the Cannizzaro reaction, in which formaldehyde and water react to methanol and formic acid, is of particular importance. As with water, formaldehyde can also react with methanol to form methylal, $CH_3—O—CH_2—O—CH_3$, and hemiformal, $CH_3—O—CH_2—OH$, from which, in turn, as in the reaction of methylene glycol to give polyoxymethylene, higher hemiformals can be formed. Other reactions that have been observed in aqueous formaldehyde solutions include the Tischenko reaction, which leads to methyl formate and the decomposition of formaldehyde to give methanol and carbon monoxide. In modeling the vapor-liquid phase equilibrium for the formaldehyde-water system, the need to keep the complexity of calculating the equilibria within acceptable limits necessarily restricts one to the most important chemical reactions. Since in most industrial applications the temperature is within the range between room temperature and about 400 K, the decomposition reaction may be disregarded. The formation of methylal and hemiformal may likewise be disregarded unless methanol is intentionally added to the aqueous formaldehyde solution. It similarly proved possible to leave unconsidered the Cannizzaro reaction as well as the Tischenko reaction. Therefore, the present model is based on the assumption that a mixture of formaldehyde and water, aside from these two substances, additionally only contains methylene glycol and a number of polyoxymethylenes. Methylene glycol cannot be prepared in pure form, yet its existence in liquid and gaseous formaldehyde-water mixtures has repeatedly been demonstrated by experiment (Walker, 1964, pp. 52–81). As the boiling points of the polyoxymethylenes are rather high, disregarding these substances in the gas phase is justified. The description is therefore based on the assumption that the gaseous phase above an aqueous formaldehyde solution only comprises the molecular substances water, formaldehyde, and methylene glycol, while the liquid phase additionally only contains polyoxymethylenes.

1. Formation of Methylene Glycol
$CH_2O + H_2O \rightleftharpoons HO-CH_2-OH$

2. Formation of Polyoxymethylene (n≥2)
$HO-(CH_2O)_{n-1}-H + HO-CH_2-OH \rightleftharpoons HO-(CH_2O)_n-H + H_2O$

3. Cannizzaro - Reaction
$2\,CH_2O + H_2O \rightleftharpoons CH_3OH + HCOOH$

4. Formation of Methylal
$2\,CH_3OH + CH_2O \rightleftharpoons CH_3O-CH_2-OCH_3 + H_2O$

5. Formation of Hemiformal
$CH_3OH + CH_2O \rightleftharpoons CH_3O-CH_2-OH$

6. Formation of higher Hemiformals (n≥2)
$CH_3O-(CH_2O)_{n-1}-H + CH_3O-CH_2-OH \rightleftharpoons CH_3O-(CH_2O)_n-H + CH_3OH$

7. Tischenko - Reaction
$HO(CH_2O)_2H \rightleftharpoons HCOOCH_3 + H_2O$

8. Decomposition (T/K ≥ 420)
$2\,CH_2O \rightleftharpoons CH_3OH + CO$

Figure 1. Chemical reactions in aqueous solutions of formaldehyde.

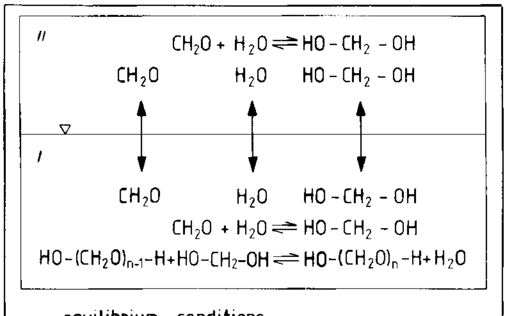
Figure 2 shows in schematic form the resulting model for the vapor-liquid equilibrium. Accordingly, the mass balance is made up of three physical and a number of chemical equilibria of which only that of methylene glycol formation appears in both phases. Since at temperatures up to 380 K the pressure above the liquid mixture rarely exceeds atmospheric pressure, and even at temperatures up to 420 K it only rises to about 500 kPa, the physical interactions in the gas phase and the effect of pressure on the fugacity and activity of any component in the liquid phase are disregarded. As a result, the thermodynamic equilibrium within the binary system formaldehyde-water is described as follows:

Physical equilibria:

Formaldehyde $p^s_{FA} x_{FA} \gamma_{FA} = P y_{FA}$ (1)

Water $p^s_w x_w \gamma_w = P y_w$ (2)

Methylene glycol $p^s_{MG} x_{MG} \gamma_{MG} = P y_{MG}$ (3)



equilibrium conditions

mech. $p' = p'' = p$

therm. $T' = T'' = T$

phys. $f'_{FA} = f''_{FA}$

$f'_W = f''_W$

$f'_{MG} = f''_{MG}$

chem. $\frac{f'_{MG} \cdot p^*}{f'_{FA} \cdot f'_W} = K_1(T) = \frac{f''_{MG} \cdot p^*}{f''_{FA} \cdot f''_W}$

$\frac{f'_n \cdot f'_W}{f'_{n-1} \cdot f'_{MG}} = K_n(T) \quad (n \geq 2)$

Figure 2. Scheme for modeling VLE in a binary mixture of formaldehyde and water.

Chemical equilibria:

$$\text{Gas phase} \quad K_1(T) = \frac{y_{MG} p^{\phi}}{y_w y_{FA} P} \tag{4}$$

$$\text{Liquid phase} \quad K_1(T) = \frac{p^s_{MG} p^{\phi}}{p^s_w p^s_{FA}} \frac{x_{MG}}{x_w x_{FA}} \frac{\gamma_{MG}}{\gamma_w \gamma_{FA}} \tag{5}$$

$$K^*_n(T) = \frac{x_n x_w}{x_{n-1} x_{MG}} \frac{\gamma_n \gamma_w}{\gamma_{n-1} \gamma_{MG}}; \quad 2 \leq n \leq n_{\max} \tag{6}$$

Accordingly, the evaluation of these equations requires the following quantities:

- The vapor pressures of water, formaldehyde, and methylene glycol
- The maximum number, $n_{\max}$, of chemical reactions to be considered
- The chemical equilibrium constants K_1 and K^*_n
- The activity coefficients

The activity coefficients are described using the UNIFAC group contribution method. Table 1 indicates the method adopted in the present paper for dividing the components into groups. Water and methylene glycol are treated as autonomous groups; formaldehyde is regarded as a CH_2O group within polyoxymethylene. The polyoxymethylenes are split into $(N - 1)$ CH_2O groups, a OH group and a CH_2 group. The formaldehyde-water system is made up of five groups. The number of necessary binary interaction parameters is 20, of which 12 are given in the literatue (Gmehling et al., 1982).

During the development of the model it proved also that at formaldehyde concentrations of up to 70 mol % the maximum number of chemical reactions to be regarded did not surmount $n_{\max} = 30$.

As the vapor pressures of pure water and of molecular formaldehyde are available (Reid et al., 1977, pp. 632–634), the only parameters in the model that still need to be known are:

- Vapor pressure of methylene glycol
- Eight UNIFAC parameters (for interactions in which methylene glycol is involved)
- Equilibrium constants $K_1(T)$ and $K^*_n(T)$; $n = 2, \ldots, 30$

Table 1. UNIFAC Data for Components in Aqueous Formaldehyde Solutions

Table 1a. UNIFAC Groups

Substance	Groups	Remarks
Water	H_2O	—
Formaldehyde	CH_2O	Same as in polyoxymethylene
Methylene glycol	$CH_2(OH)_2$	–
Polyoxymethylene $HO—(CH_2O)_n—H$	$(n - 1)$ $—CH_2O—$ 2 $—OH$ 1 $—CH_2—$	—
Methanol	CH_3OH	—
Hemiformal $HO—(CH_2O)_n—CH_3$	$(n - 1)$ $—CH_2O—$ 1 $CH_3O—$ 1 $—CH_2OH$	Same as in polyoxymethylene Ether Methanol
Trioxane	$(CH_2O)_3$	—

Table 1b. UNIFAC Size and Surface Parameters

Group No.	Group	Size Parameter r	Surface Parameter q
1	$—OH$	1.0	1.2
2	$—CH_2O—$	0.9183	0.78
3	$—CH_2—$	0.6744	0.54
4	H_2O	0.9200	1.40
5	$CH_2(OH)_2$	2.6744	2.94
6	CH_3OH	1.4311	1.432
7	$CH_3O—$	1.1450	1.088
8	$—CH_2OH$	1.2044	1.124
9	$(CH_2O)_3$	2.754	2.34

Equilibrium constants for the chemical reactions

The equilibrium constant $K_1(T)$ for the formation of methylene glycol in the gas phase was determined by Hall and Piret (1949) and by Kogan (1979b) from gas density measurements. These results are compared with each other in Figure 3. Kogan's measurements cover a temperature range of 20 K and are systematically below the results of Hall and Piret, which cover the significantly wider range from about 320 to 420 K. In the course of developing the model, it was found that the results of Hall and Piret gave a slightly better presentation of vapor-liquid equilibria. The subsequent considerations are therefore based on the temperature dependence of $K_1(T)$ indicated by these authors:

$$\ln K_1 = -22.57 + 7{,}368/(T/K) \tag{7}$$

Data on the distribution of formaldehyde in aqueous solution over the various kinds of polyoxymethylene are available from nuclear magnetic resonance spectroscopy studies by Koberstein et al. (1971) and by Skell and Suhr (1961). In addition, it is known from measurements of the ultraviolet absorption in formaldehyde solutions (Walker, 1964, pp. 55–61) that the proportion of molecular formaldehyde is negligible small. Koberstein et al. were able to describe their measurements, obtained at temperatures between 310 and 370 K for formaldehyde concentrations of up to 70 wt. %, by means of

$$K_x = \frac{x_n x_w}{x_{n-1} x_{MG}} = 3.77. \tag{8}$$

This result also gives good representations of the measurements by Skell and Suhr and of the average molecular weights of formaldehyde in aqueous solution determined from cryoscopic measurements by Auerbach and Barschall and by Iliceto (Walker, 1964, p. 62). The chemial equilibrium constants K^*_n were therefore determined as follows: The above-mentioned number for K_x was used to calculate the distribution of the polyoxymethylenes for a given overall formaldehyde content in water, then the UNIFAC model was applied to determine the activity coefficients for this distribution at a given temperature, resulting in K^*_n as indicated in Eqs. 5 and 6. This calculation was repeated for various overall formaldehyde contents at a given temperature. All calculations were repeated for various temperatures, and the numerical values for $K^*_n(T)$ were then smoothed as a function of the chain length n and the temperature T. A subsequent comparison of calculated and measured vapor-liquid

Table 1c. UNIFAC Interaction Parameter $A_{i,j}/K$

	j								
i	1	2	3	4	5	6	7	8	9
1	—	28.06*	156.4*	353.5*	353.5	−137.1*	28.06	−137.1	28.06
2	237.7*	—	83.36*	240.0	240.0	339.7	0.0	339.7	0.0
3	986.5*	251.5*	—	1,318.0*	1,318.0	697.2*	251.5	697.2	251.5
4	−229.1*	−149.0	300.0*	—	0.0	289.6*	−149.0	289.6	−92.9
5	−229.1	−149.0	300.0	0.0	—	289.6	−149.0	289.6	−92.9
6	249.1*	−180.6	16.51*	−181.0*	−181.0	—	−180.6*	0.0	n.n.
7	237.7	0.0	83.36	240.0	240.0	339.7*	—	339.7	n.n.
8	249.1	−180.6	16.51	−181.0	−181.0	0.0	−180.6	—	n.n.
9	237.7	0.0	83.36	385.0	385.0	n.n.	n.n.	n.n.	—

*From Gmehling et al. (1982); n.n., not needed in this work.

equilibria showed that at low temperatures somewhat lower values of K_x give improved representation of the phase equilibrium. The thermodynamic equilibrium constants used for all further calculations are:

$$\ln K_2^* = -7.0265 + \frac{6,844.1}{T/K} - \frac{1.39179\ 10^6}{(T/K)^2} \tag{9}$$

and for $n \geq 3$:

$$\ln K_n^* = -7.9316 + \frac{0.32}{n} + \frac{7,132.97 - 238.9/n}{T/K} - \frac{1.39179\ 10^6}{(T/K)^2}. \tag{10}$$

A comparison of the average molecular weight of formaldehyde in aqueous solution calculated on the basis of these constants with results from the literature shows that these numerical values for K_n^* give average molecular weights that are too low. The reason for the necessary shift is presumably the insufficient dependence on temperature of the activity coefficients calculated with the UNIFAC model, which had to be compensated for by correcting the numerical values for K_x (refer to supplementary material).

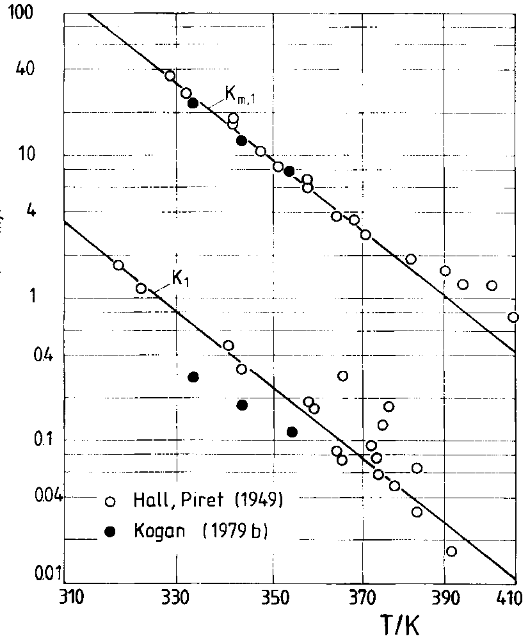


Figure 3. Equilibrium constant for the formation of methylene glycol, K_1, and hemiformal, $K_{m,1}$.

UNIFAC interaction parameters

In the UNIFAC model there are eight unknown interaction parameters $A_{i,j}$ between the groups *i* and *j*, either of which represents methylene glycol. To reduce the number of parameters in the model that require fitting, an attempt was made to estimate these parameters. Methylene glycol can be regarded as the second representative of the series of diol homologs, the first representative being hydrogen peroxide and the third ethanediol.

Table 2 gives literature data for the activity coefficients of some diols in water at infinite dilution, put together from vapor-liquid equilibrium measurements by various authors. These activity coefficients are all close to unity, so that the corresponding

Table 2. Activity Coefficients of Some Diols in Water at Infinite Dilution

Diol	Temp., *T* K	γ^∞
H_2O_2*	303.15	0.5
	318.15	0.35
	333.15	0.72
1,2 Ethanediol**	299.1	0.87
	311.4	1.19
	324.8	1.19
	342.7	0.86
	366.9	0.92
1,2 Propanediol**	288.15	1.22
	293.15	1.12
	298.15	0.83
	299.05	1.14
	299.05	1.20
	303.15	0.91
	308.15	1.06
	311.35	0.61
	318.15	1.13
	323.15	1.20
	324.65	1.69

*Giquère and Maass (1940)
**Gmehling and Onken (1977)

numerical value for methylene glycol in water may likewise be assumed to be unity. In the UNIFAC model the interaction parameters with methylene glycol were therefore assumed to have the same numbers as the corresponding interaction parameters with water:

$$A_{MG,j} = A_{W,j} \quad A_{j,MG} = A_{j,W}. \tag{11}$$

The comparisons subsequently performed between calculated and measured vapor-liquid equilibria revealed that the representation of the measurements is improved slightly when the literature values for the interaction parameters between water and the CH_2O group are changed to $A_{CH_2O,w} = 240$ K and $A_{w,CH_2O} = -149$ K, respectively. All UNIFAC parameters used in the modeling are given in Table 1 together with the size and shape parameters for the various groups.

Vapor pressure of methylene glycol

The only unknown quantity left in the model is the vapor pressure of methylene glycol. As methylene glycol cannot be prepared in pure form, and hence direct measurement is impossible, the vapor pressure was determined from measurements of the vapor-liquid equilibrium for the system formaldehyde-water. For a given temperature T and overall mole fraction $\tilde{x}_{FA}$ of formaldehyde, Eq. 8 was used to calculate the true mole fractions in the liquid phase. From the UNIFAC model the activity coefficients were derived. Combining these results with the phase equilibrium conditions for water and methylene glycol, Eqs. 2 and 3, the chemical equilibrium in the gas phase, Eq. 4, and the mass balance in the gas phase

$$\tilde{y}_{FA} = \frac{y_{FA} + y_{MG}}{1 + y_{MG}} \tag{12}$$

from each experimental triple T, $\tilde{x}_{FA}$, and $\tilde{y}_{FA}$—without using the experimental result for the pressure—one numerical value for the vapor pressure of methylene glycol was determined. The numerical values obtained for a fixed temperature were averaged and $p^s_{MG}(T)$ was then smoothed in the form of an Antoine equation.

The selection of vapor-liquid equilibrium measurements that were suitable for calculating p^s_{MG} presented problems, since the measurements reported in the literature exhibit considerable discrepancies. Therefore the vapor-liquid equilibrium was measured at 323.15, 343.15, and 363.15 K on solutions containing up to 40 wt. % of formaldehyde in the liquid phase (Maurer, 1982; cf. Table 3). The results are in good agreement with measurements by Kogan et al. (1977) and Brandani et al. (1980). As Brandani et al. did not specify the composition of the gas phase, the vapor pressure determination was based only on the results obtained by Kogan et al. within the temperature range between 313 and 363 K for formaldehyde concentrations in the liquid phase of up to about 70 wt. %. Table 4 indicates the parameters for the Antoine equation of methylene glycol. This vapor pressure curve gives an atmospheric pressure boiling point for methylene glycol of 452 K (cf. Figure 4). On interpolating the atmospheric pressure boiling points of the homologous series of diols, a value between 450 and 451 K is obtained for methylene glycol.

Table 3. Experimental and Calculated Results for VLE in Aqueous Solutions of Formaldehyde

Temp. T/K	$\tilde{x}_{FA}$, mol %	$\tilde{y}_{FA}$, mol % Exp.	$\tilde{y}_{FA}$, mol % Calc.	Pressure, P kPa Exp.	Pressure, P kPa Calc.
323.15	2.76	1.57	1.60	12.24	12.20
	3.17	1.42	1.81	12.24	12.17
	11.6	4.48	5.50	11.81	11.75
	11.9	5.84	5.61	11.80	11.73
	12.8	4.79	5.94	11.68	11.68
	25.5	10.8	10.2	10.93	11.85
		$z = -11.1$		$z = -1.2$	
		$s = 19.5$		$s = 4.2$	
343.15	1.87	1.68	1.83	31.12	31.18
	3.06	2.74	2.68	31.13	31.17
	3.17	2.84	2.95	30.98	31.17
	10.75	7.58	7.88	30.72	30.81
	13.1	9.58	9.07	30.77	30.65
	21.0	13.4	12.6	30.16	29.96
	22.7	14.1	13.3	29.92	29.80
		$z = -0.6$		$z = 0.03$	
		$s = 6.1$		$s = 0.5$	
363.15	2.90	3.81	4.05	70.70	71.10
	6.13	7.13	7.44	71.35	71.70
	9.49	10.1	10.2	71.50	71.98
	13.1	12.6	12.7	71.62	72.02
	16.8	15.2	14.9	71.46	71.87
	20.9	17.8	17.0	71.29	71.53
	21.4	17.8	17.3	70.90	71.47
	30.2	22.9	21.5	69.79	70.23
		$z = 0.4$		$z = 0.6$	
		$s = 4.3$		$s = 0.6$	
363.15	9.44	—	10.2	71.58	71.98
	11.62	—	11.7	71.73	72.03
	16.67	—	14.8	71.50	71.87
	28.74	—	20.8	70.27	70.47
	28.79	—	20.8	70.26	70.47
	28.82	—	20.8	70.22	70.46
		—	—	$z = -0.4$	
		—	—	$s = 0.5$	

The vapor pressure curve yields a value of 36 kJ/mol for the heat of evaporation of methylene glycol at the atmospheric pressure boiling point, whereas the arithmetic mean of the heats of evaporation of hydrogen peroxide and ethanediol is about 48 kJ/mol. These two comparisons confirm the physicochemical assumptions on which the model is based.

Comparison of calculated and measured VLE

There are many measurements in the literature for the vapor-liquid phase equilibrium in the binary system formaldehyde-water. However, in some cases there are appreciable differences between these measurements. The following compari-

Table 4. Vapor Pressures

$\ln \frac{p^s_i}{\text{kPa}} = a_i - \frac{b_i}{T/K + c_i}$	a_i	b_i	c_i
Formaldehyde	14.4625	2204.13	− 30.15
Water	16.2886	3816.44	− 46.13
Methylene glycol	11.0768	1997.20	−142.72
Methanol	16.5725	3626.55	− 34.29
Hemiformal	18.0125	5125.0	0.0
Trioxane	15.6529	3882.57	− 35.54

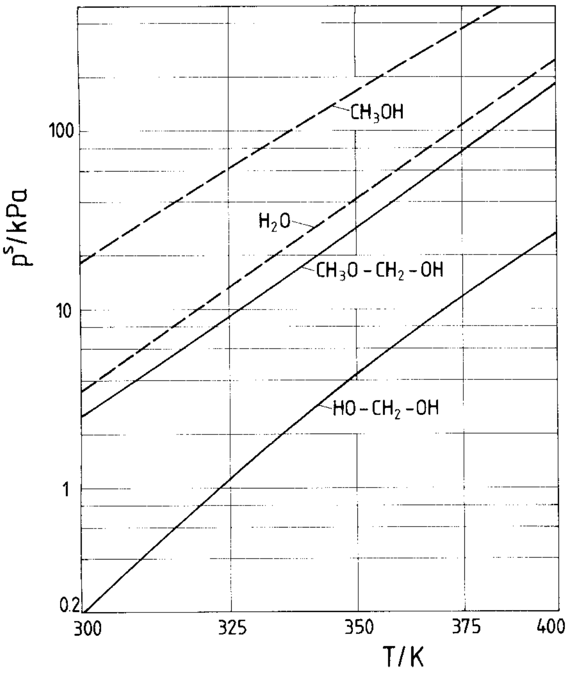


Figure 4. Vapor pressure of some pure substances.

son is mainly restricted to some of the more recent publications. Usually the calculations started from preset numbers for the temperature and the liquid phase composition, while the pressure and the gas phase composition were calculated. (For more details as well as a scheme for calculating VLE in the system formaldehyde-water system, refer to the supplementary material.)

Figures 5a–c give a comparison of the total pressures and the concentration differences $\tilde{y}$-$\tilde{x}$ calculated for 323.15, 343.15, and 363.15 K with the measurements of Kogan et al. (1977) and Brandani et al. (1980), and with our own measurements (Maurer, 1982); in addition, Tables 3 and 5 contain some numerical values for these and other comparisons. The measurements by Kogan used for determining the vapor pressure of methylene glycol are in excellent agreement with the calculated values over

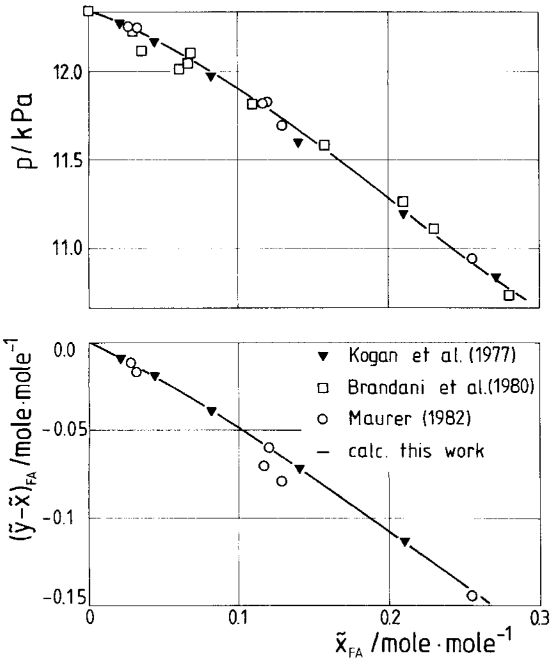


Figure 5a. VLE in aqueous solutions of formaldehyde at 323.15 K.

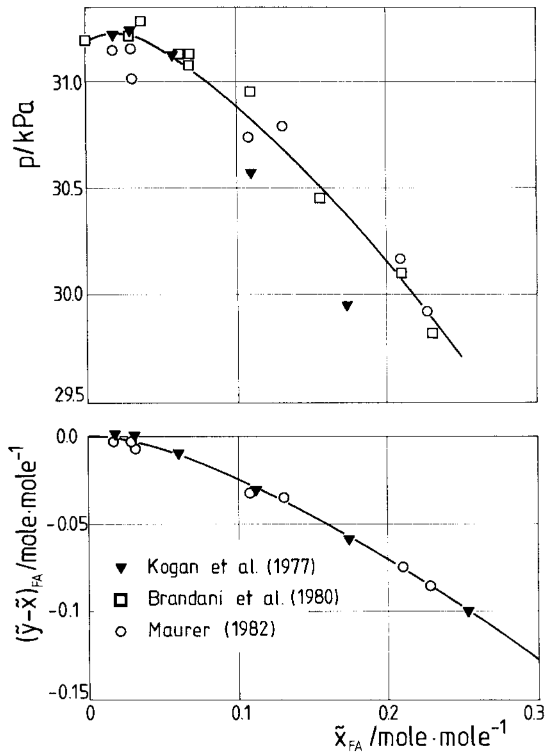


Figure 5b. VLE in aqueous solutions of formaldehyde at 343.15 K.

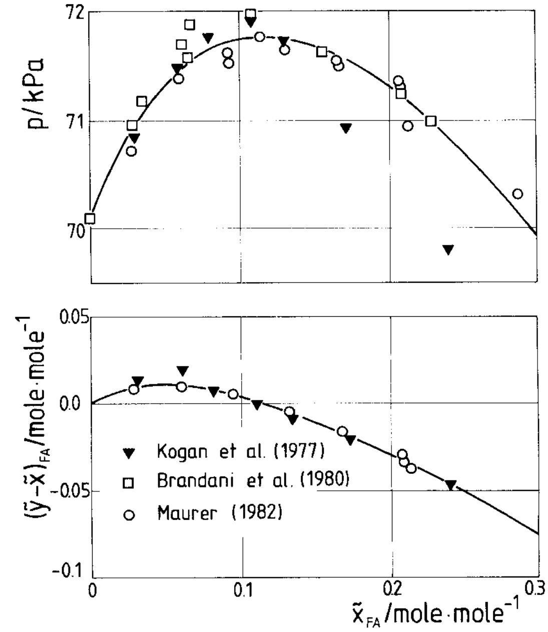


Figure 5c. VLE in aqueous solutions of formaldehyde at 363.15 K.

Table 5. Representation of Experimental VLE in the Water-Formaldehyde System

Authors	Kind of Measurement	No. of Exp. Points	Avg. Dev. in Representing		Std. Dev. in Representing	
			P	$\bar{y}_{FA}$	P	$\bar{y}_{FA}$
Brandani et al. (1980)	T, K =					
	313.15	10	0.73	—	1.07	—
	323.15	11	−0.15	—	0.42	—
	333.15	11	−0.62	—	0.81	—
	343.15	11	−0.17	—	0.27	—
	353.15	11	0.13	—	0.28	—
	363.15	11	0.28	—	0.19	—
	avg	65	0.02	—	0.57	—
Kogan et al. (1977)	T, K =					
	313.15	9	1.3	2.6	1.0	4.4
	323.15	9	0.43	2.0	0.71	4.7
	343.15	10	−0.54	2.5	0.95	4.1
	353.15	11	−0.50	0.14	1.2	3.7
	363.15	13	−0.62	−0.56	1.6	5.6
	avg	52	−0.07	1.2	1.1	4.4
Green and Vener (1955)	p, kPa =					
	101.3	12	−1.3	−12	0.59	6.5
Olevsky and Golubev (1954)	p, kPa =					
	8.0	10	1.2	−21	17	27
	13.3	10	−8.6	−17	10	6.7
	26.7	10	−8.2	−1.9	6.9	5.5
	46.7	10	−5.5	4.6	6.5	6.4
	101.3	10	1.0	−3.1	3.0	8.4
	avg	50	−0.01	−7.7	9.5	13
Olsson and Svensson (1975)	T, K =					
	353.15	6	—	−4.1	—	6.2
	373.15	8	—	−2.8	—	5.2
	393.15	8	—	−5.8	—	5.9
	403.15	8	—	−7.6	—	6.5
	avg	30	—	−5.1	—	5.9
Blazhin et al. (1977)	p, kPa =					
	304	7	−6.8	−2.1	3.3	13.9
	507	7	−7.4	−3.9	4.6	11.4

the entire concentration and temperature range, the mean relative deviation in the formaldehyde concentration in the gas phase being only 1.2% and the standard deviation 4 to 5%. The vapor pressure measurements (boiling lines) by Kogan et al. that were not used in the fit are very well represented at 313.15 and 323.15 K, but at higher temperatures the calculated values at higher formaldehyde concentrations are systematically above the measured values, the differences increasing with increasing distance from the azeotropic point and amounting to as much as 2%. However, within this range the vapor pressures reported by Kogan are virtually the same amount below the results of Brandani et al. and our own measured values, which agree with each other and with the calculated values to within a few tenths of 1%. In the case of other literature sources, the differences between measured and calculated values are only in some instances similarly small. For instance, the $\tilde{x}$, $\tilde{y}$, T measurements given by Olsson and Svensson (1975) for 353.15 K are represented to the same degree of accuracy as the measurements by Kogan. Even at temperatures as high as 400 K—that is, clearly outside the temperature range within which parameters of the model were fitted—the measurements by Olsson and Svensson are represented well. Isobaric literature data were also compared with results calculated starting from preset numbers for the pressure and the overall composition of the liquid phase. As an example Figure 6 shows such a comparison for atmospheric pressure. Boiling points reported by different authors differ from each other by up to 3. Calculated boiling points agree best with the results by Green and Vener (1955), the maximum deviation being less than 0.5 K.

The Binary System Formaldehyde-Methanol

As formaldehyde reacts with methanol in a similar manner as with water (Figure 1), the vapor-liquid equilibrium in the formaldehyde-methanol binary system is described in essentially the same way as in the formaldehyde-water system. Therefore all relations shown in Figure 2 can also be used here, when water, methylene glycol, and the polyoxymethylenes are replaced by methanol, hemiformal ($CH_3—O—CH_2—OH$), and the higher hemiformals [$CH_3—O—(CH_2O)_n—H$], respectively. Consequently also, the chemical equilibrium constants K_i are replaced by $K_{m,i}$, the corresponding constants for the reactions describing the formation of all hemiformals. Applying exactly the same approximations as discussed previously finally results in the following relationships:

Physical Equilibria:

Formaldehyde $$p^s_{FA} x_{FA} \gamma_{FA} = P y_{FA} \quad (1)$$

Methanol $$p^s_{Me} x_{Me} \gamma_{Me} = P y_{Me} \quad (13)$$

1. Hemiformal $$p^s_{HF} x_{HF} \gamma_{HF} = P y_{HF} \quad (14)$$

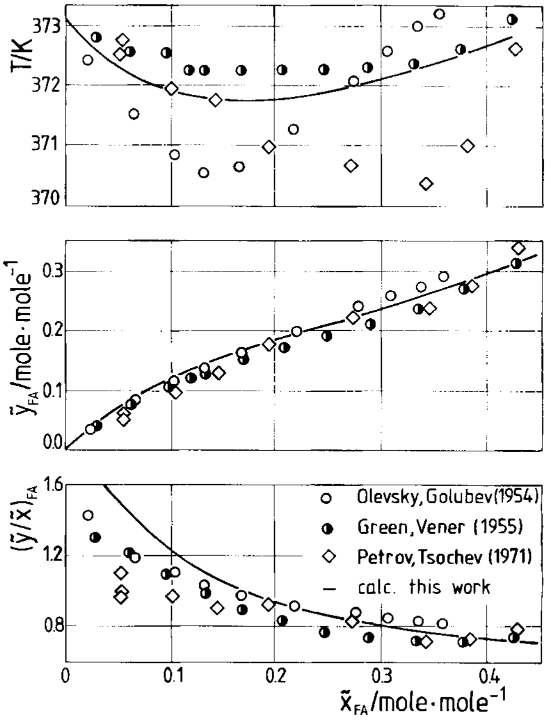


Figure 6. VLE in aqueous solutions of formaldehyde at 101.3 kPa.

Chemical Equilibria:

$$\text{Gas phase} \quad K_{m,1}(T) = \frac{y_{HF}p^{\phi}}{y_{Me}y_{FA}p} \tag{15}$$

$$\text{Liquid phase} \quad K_{m,1}(T) = \frac{p^{s}_{HF}p^{\phi}}{p^{s}_{Me}p^{s}_{FA}} \frac{x_{HF}}{x_{Me}x_{FA}} \frac{\gamma_{HF}}{\gamma_{Me}\gamma_{FA}} \tag{16}$$

$$K^{*}_{m,n}(T) = \frac{x_{m,n}x_{Me}}{x_{m,n-1}x_{HF}} \frac{\gamma_{m,n}\gamma_{Me}}{\gamma_{m,n-1}\gamma_{HF}}; \quad 2 \le n \le n_{\max} \tag{17}$$

In the UNIFAC method for calculating the activity coefficients methanol is regarded as an independent group, the lowest hemiformal is split into an ether group (CH_3—O—) and a methanol-like group (—CH_2—OH), and the higher hemiformals into an ether group, $(n - 1)$ formaldehyde groups (—CH_2O—), and the methanol-like group (—CH_2—OH) (cf. Table 1). The size and shape parameters of these groups were taken from the literature (Gmehling et al., 1982) with the exception of (—CH_2—OH). As no literature data are available, the parameters for this group were determined from data for methanol and the difference in numerical data between the CH_3—and the —CH_2— group.

To determine the interaction parameters, it was assumed that the formaldehyde group and the ether group, on the one hand, and the methanol group and the methanol-like group, on the other, do not differ. This meant that all parameters could be taken from the literature (Gmehling et al., 1982; cf. Table 1).

For the equilibrium constant of the formation of hemiformal in the gas phase, Kogan (1979a) has given an equation that agrees very well with earlier measurements by Hall and Piret (1949) and was therefore adopted:

$$\ln K_{m,1} = -16.2707 + 6{,}462.14/(T/K). \tag{18}$$

As shown in Figure 3, the equilibrium constant for the formation of hemiformal is much larger than that for methylene glycol, resulting in very different amounts of formaldehyde present as monomers in gaseous mixtures of formaldehyde with water or methanol. For example, at around 350 K and 26.5 kPa a binary mixture with an overall mole fraction of 30% formaldehyde contains 97 or 44% of the formaldehyde as monomers when water or methanol is the second component.

To determine the equilibrium constants of the formation of higher hemiformals, nuclear resonance spectroscopy measurements by Kogan (1979b) were used in the same procedure as described earlier for the formation of polyoxymethylene, resulting in:

$$\ln K^{*}_{m,2} = -2.0973 - 49.15/(T/K) \tag{19}$$

$$\ln K^{*}_{m,n} = -1.8204 + 0.555/n - 53/(T/K); \quad n = 3 \div 30; \tag{20}$$

The ratios of mole fractions of hemiformal (CH_3O—CH_2—OH) to formaldehyde (overall) and of real to overall mole fraction of methanol calculated from these equations, agree well with the results of spectroscopic investigations by Kogan (1979a), at overall formaldehyde contents ranging to more than 50 mol %; only at even higher formaldehyde concentrations are significant deviations observed, though essentially only in respect of the methanol concentration (see supplementary material).

The vapor pressure of hemiformal p^{s}_{HF} was again the only quantity that had to be fitted to some experimental vapor-liquid phase equilibrium measurements. Data reported by Kogan and Ogorodnikov (1980a) for the binary system formaldehyde-methanol were used in these calculations. The results are given, together with the vapor pressure of methanol taken from the literature (Reid et al., 1977, p. 635), in Table 4. As is shown in Figure 4, the vapor pressure of hemiformal differs from that of methanol in a similar manner as the vapor pressure of methylene glycol from that of water.

Comparison of calculated and measured VLE in the system formaldehyde-methanol

Figures 7a to 7c show a comparison of measurements by Kogan and Ogorodnikov (1980a) at 333.15, 343.15, and 353.15 K (formaldehyde concentration up to about 70 mol %, pressure from 20 to 170 kPa) which, except for the measured value of the pressure, were used to determine the vapor pressure of the lowest hemiformal, with calculated results. For the calculations, the temperature and overall formaldehyde content in the liquid were preset and the pressure and composition of the gas phase were calculated. At 333.15 K, the standard deviation in the pressure is 3.1% (corresponding to less than 1 kPa), at 343.15 and 353.15 K it is 6.8% (corresponding to about 2 and 3 kPa, respectively). These numerical data are essentially due to deviations at concentrations above about 50 mol % formaldehyde. At lower concentrations, the agreement between calculated and measured pressures is distinctly better. Regarding the formaldehyde content of the gas phase, the standard deviation at 333.15 K is 7.1% (corresponding to about 0.0075 mol/mol), at 343.15 it

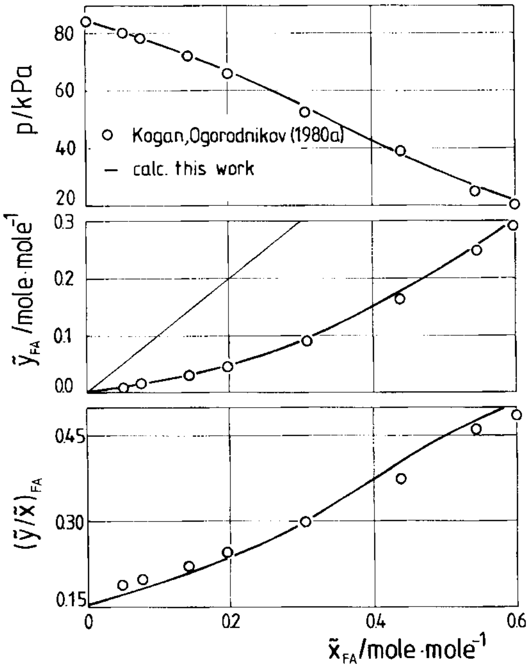


Figure 7a. VLE in a formaldehyde-methanol mixture at 333.15 K.

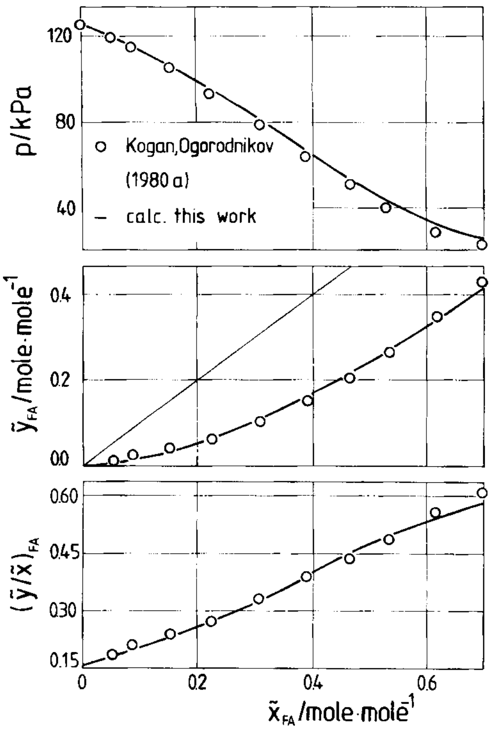


Figure 7b. VLE in a formaldehyde-methanol mixture at 343.15 K.

is 3.5% (again corresponding to about 0.0075 mol/mol), and at 353.15 it is 7.0% (corresponding to about 0.018 mol/mol). Figure 8 shows a comparison with some isobaric measurements at 26.7 and 101.3 kPa, with the pressure and formaldehyde content of the liquid phase being the preset data in the calculation. The data given by Olevsky and Golubev (1954) deviate systematically from the results obtained by Kogan and coworkers (Blazhin et al., 1976). As was also the case for the formaldehyde-water system, so here again the boiling points and dew points measured by Olevsky and Golubev are markedly higher than the results of Kogan et al., which agree well with those obtained from the calculation model. At 26.7 kPa the mean deviations (arithmetic means of the contributions of the deviations) are only 1.3 K in respect to the boiling point and 0.015 mol/mol in respect to the formaldehyde content of the gas phase, while at atmospheric pressure the corresponding numbers are only 1.5 K and 0.0016 mol/mol.

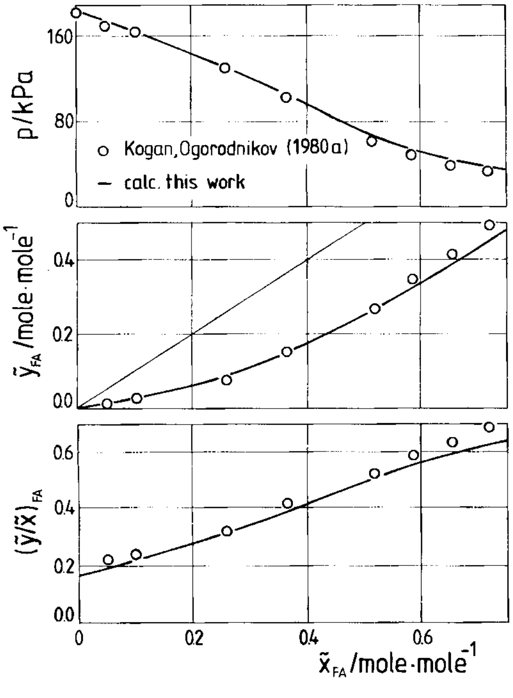


Figure 7c. VLE in a formaldehyde-methanol mixture at 353.15 K.

These comparisons demonstrate that the model accurately represents the vapor-liquid equilibrium in the system formaldehyde-methanol.

The Ternary Mixture of Formaldehyde, Water, and Trioxane

Extension of the model

The modeling approach presented before can be extended to multicomponent systems that contain chemically inert components, in addition to formaldehyde and water. This is demonstrated by considering the industrially important ternary mixture of formaldehyde, water, and trioxane.

On adding to a binary mixture of formaldehyde and water a chemically inert substance A the scheme for modeling the vapor-liquid equilibrium shown in Figure 2 has to be supplemented by a physical equilibrium condition similar to that for formaldehyde, water, and methylene glycol, indicating that the added substance is present in both phases:

$$f'_A = f''_A. \tag{21}$$

Disregarding the Poynting correction and all gas phase nonidealities, this equation can be rearranged to:

$$p^s_A \cdot x_A \cdot \gamma_A = P \cdot y_A. \tag{22}$$

Equations 1, 2, 3, 4, 22, and 5 and 6 together with the components stoichiometric or overall mole fraction terms derived from mass conservation:

$$\tilde{x}_{FA} = \frac{x_{FA} + \sum_{i=1}^{\infty} i \cdot x_i}{1 + \sum_{i=1}^{\infty} i \cdot x_i} \tag{23}$$

$$\tilde{x}_A = \frac{x_A}{1 + \sum_{i=1}^{\infty} i \cdot x_i} \tag{24}$$

$$\tilde{x}_w = 1 - \tilde{x}_{FA} - \tilde{x}_A \tag{25}$$

$$\tilde{y}_{FA} = \frac{y_{FA} + y_{MG}}{1 + y_{MG}} \tag{26}$$

$$\tilde{y}_A = \frac{y_A}{1 + y_{MG}} \tag{27}$$

$$\tilde{y}_w = 1 - \tilde{y}_{FA} - \tilde{y}_A \tag{28}$$

($i \hat{=}$ polyoxymethylene)

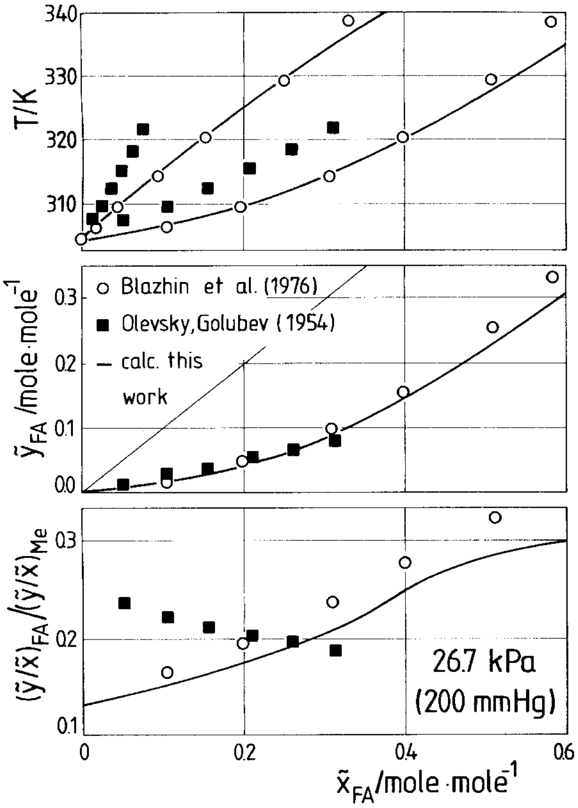


Figure 8a. VLE in a formaldehyde-methanol mixture at 26.7 kPa.

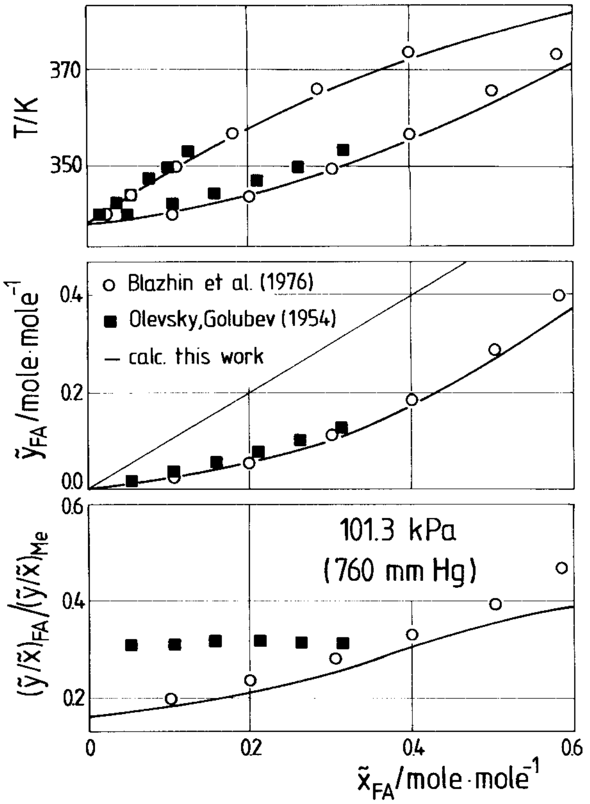


Figure 8b. VLE in a formaldehyde-methanol mixture at 101.3 kPa.

describe the distribution of formaldehyde, water, and the inert component A between the two phases.

In addition to the data given before, the following quantities are required:

- The vapor pressure of the inert component A:p^s_A
- The splitting of this component into structure groups, and for each structure group the UNIFAC size and shape parameters (r, q)
- The UNIFAC parameters for the interactions of the newly added structure groups with the above-mentioned five groups of the formaldehyde-water system.

If further chemically inert components are included in the mixture, the extension and the additional data needed can be decided analogously.

Procedure illustrated for the ternary system formaldehyde-water-trioxane

The Vapor Pressure of Trioxane. Data on the vapor pressure of pure trioxane between about 360 and 400 K as measured by Auerbach and Barschall at the start of this century and as measured at Dupont can be found in Walker (1964, p. 193). More recently, Serebrennaya and Byk (1973) have published measurements for the temperature range between 328 and 388 K. The Antoine equation given in Table 4 reproduces these values with a standard deviation of 1.4% in the pressure.

UNIFAC Parameters for Trioxane. In the modeling, trioxane is treated as an independent group. Since trioxane is a ring-shaped molecule of three CH_2O groups, the numerical values for the size and shape parameters of the CH_2O group were tripled to obtain the corresponding sizes for trioxane (Table 1b).

A total of 10 interaction parameters $A_{i,j}$ need to be fixed for the formaldehyde-water-trioxane system. To obtain a check on whether the model obtained for formaldehyde-water could be extended in a simple manner, these parameters were estimated or were determined from vapor-liquid equilibrium measurements for the water-trioxane system. Thus, no measurements on ternary mixtures were used. The interaction parameters between trioxane on the one hand and the group of OH—, CH_2O—, CH_2— on the other hand were approximated to those parameters where the place of trioxane is taken by the —CH_2O group (Table 1c). As in the case of the formaldehyde-water system, the parameters for the interactions in which methylene glycol is involved were approximated by the corresponding parameters where water is involved ($A_{\text{trioxane},MG} = A_{\text{trioxane},w}$; $A_{MG,\text{trioxane}} = A_{w,\text{trioxane}}$).

The only unknowns that are thus left are the two parameters for interactions between water and trioxane. These parameters were determined from measurements of the vapor-liquid equilibrium in the water-trioxane system. The only data described in the literature are equilibrium data measured under ambient pressure. Duras (1967) only measured the boiling line curve and used it to calculate, by means of the van Laar equation, the activity coefficients and the composition of the gas phase. Since, moreover, his results are available only in graph form, they were not included in the valuation. Serebrennaya and Byk (1966) and Kovac and Ziak (1970) have measured the concentrations in the two coexisting phases. By means of the maximum likelihood method, the measurements were used to determine the UNIFAC parameters $A_{\text{trioxane},w}$ and $A_{w,\text{trioxane}}$ (Table 1c). In Figure 9 a and b, calculated and measured equilibrium diagrams

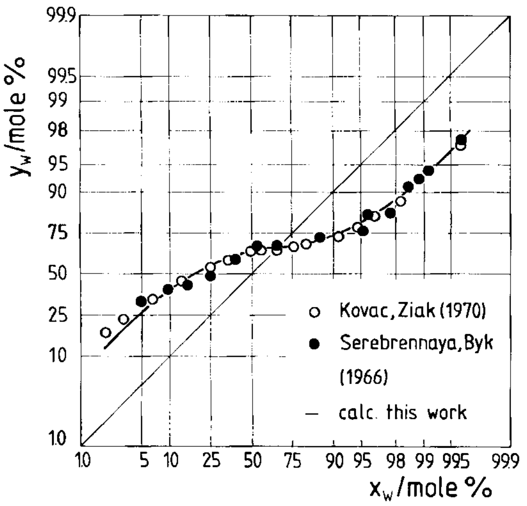


Figure 9a. Equilibrium diagram for water-trioxane at 101.3 kPa.

and boiling lines are compared; for better resolution the concentration is plotted logarithmically. The measured concentrations are represented well by the UNIFAC model over the entire range that has been studied; however, there are systematic deviations by up to 1 K in the boiling line, especially around the azeotropic point.

Comparison between calculated and measured vapor-liquid phase equilibrium

From preset numbers for the temperature and the overall composition of the liquid phase the overall composition of the gas phase and the pressure were calculated and compared with data on VLE in the ternary mixture of formaldehyde, water, and trioxane for atmospheric pressure reported by Petrov et al. (1971). Experimental results by Kovac and Ziak (1970) were not used for comparison, as these authors indicate only trioxane but no formaldehyde concentrations in the gas phase. From experience in operating distillation equipment the reliability of these data seemed to be highly questionable. Table 6 shows some typical results of the comparison. The calculated formaldehyde content of the gas phase is about three times the measured value (average taken over all the 50 measured points indicated by Petrov et al.). In the case of trioxane, the measured values for the concentration in the gas phase are on average almost twice the calculated values. The calculated pressures are overwhelmingly (45 out of 50 measured values) below the measured values, the standard deviation being just below 4%.

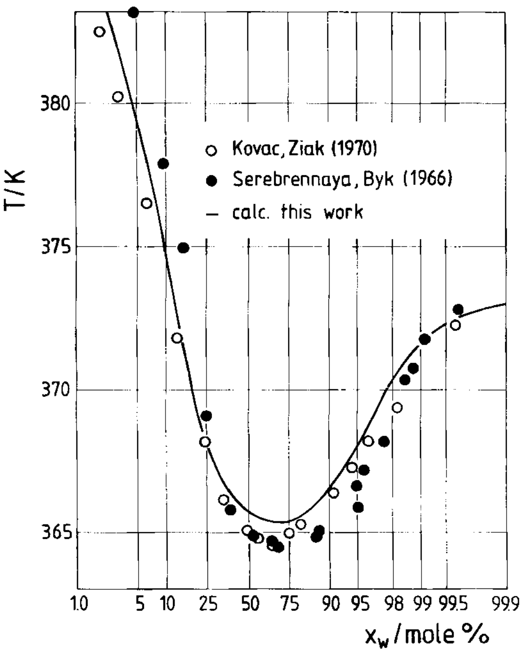


Figure 9b. Boiling line for water-trioxane at 101.3 kPa.

Table 6. VLE in the System Formaldehyde-Water-Trioxane

			$(\tilde{y}/\tilde{x})_{FA}$		$(\tilde{y}/\tilde{x})_{\mathrm{Triox}}$		P
T/K	$\tilde{x}_{FA}$	$\tilde{x}_{\mathrm{Troix}}$	Exp.	Calc.	Exp.	Calc.	kPa Calc.
370.1	0.1665	0.0525	0.569	0.909	6.03	4.19	99.2
366.0	0.0187	0.3398	0.0374	0.740	1.84	1.86	99.2
370.2	0.2223	0.0669	0.437	0.792	5.08	3.78	100.7
368.7	0.2297	0.1209	0.371	0.664	3.68	3.06	98.7
371.2	0.4685	0.0115	0.508	0.752	14.9	4.50	97.6
369.2	0.3815	0.1094	0.370	0.585	3.38	3.07	97.9
373.7	0.0587	0.0139	0.513	1.467	5.45	5.86	107.6
369.9	0.0747	0.1943	0.108	0.773	2.86	2.61	108.3
368.4	0.4300	0.1927	0.271	0.486	2.51	2.41	97.5

Comparison of some results reported by Petrov et al. (1971) for 101.325 kPa (760 mm Hg).

Concentrations in g/g.

Since the skepticism concerning the measurements by Petrov et al. was also reinforced by a comparison of the phase equilibrium values given by Tsochev and Petrov (1973) for the formaldehyde-water system with the data of other authors (Figure 6), new measurements of the vapor-liquid equilibrium on the formaldehyde-water-trioxane system were carried out.

Results of new measurements and comparison with calculated equilibria

In the experiments, a liquid feed mixture of known concentration was continuously partially evaporated in a special kind of thin-film evaporator. After separation from the liquid the gas phase was condensed; the two liquids were then analyzed. The formaldehyde content was determined by means of the sodium sulfite method, while the trioxane content was determined by using sulfuric acid to depolymerize trioxane to formaldehyde, which was then determined in a second formaldehyde analysis. To check whether the phase equilibrium had been attained, especially whether the distribution of the polyoxymethylenes was stable, the evaporatoin ratio—i.e., the ratio of the volume of the condensed gas phase to the volume of the unevaporated liquid phase—was varied in preliminary experiments. This was to make certain that the evaporation ratios in the subsequent measurements were sufficiently small to ensure that the time for passing through the apparatus was long enough for the new equilibrium to become established. In total, 26 measured points were recorded close to the atmospheric pressure at temperatures between about 366 and 370 K. The formaldehyde concentrations in the liquid ranged from about 4 to 46 wt. %, and the triox-

Table 7. Experimental and Calculated Results for VLE in the Ternary System Formaldehyde-Water-Trioxane

Temp.	Liquid Phase		$(\tilde{y}/\tilde{x})_{FA}$		$(\tilde{y}/\tilde{x})_{\text{Triox}}$		Press., P kPa	
T/K	$\tilde{x}_{FA}$	$\tilde{x}_{\text{Troix}}$	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
369.69	4.23	8.47	1.17	1.07	3.93	4.08	100.5	99.3
366.53	9.49	23.31	0.645	0.663	2.42	2.31	100.7	97.5
369.03	9.58	11.37	0.812	0.854	3.52	3.41	101.9	99.8
366.41	10.14	20.27	0.659	0.679	2.62	2.52	99.2	95.6
370.01	11.35	7.76	0.894	0.926	4.17	3.90	102.1	100.8
368.41	19.51	9.65	0.716	0.738	4.08	3.42	99.2	96.3
369.71	23.51	7.40	0.707	0.756	4.11	3.65	100.0	99.5
368.48	24.17	10.73	0.676	0.673	3.46	3.21	99.7	97.0
366.61	26.73	22.93	0.496	0.515	2.27	2.21	100.2	96.0
369.08	37.07	11.96	0.538	0.577	3.36	2.97	100.4	98.4
367.92	41.69	23.59	0.450	0.464	2.30	2.17	101.2	97.6
369.91	41.97	9.32	0.603	0.596	3.58	3.23	101.3	99.1
368.28	46.62	21.69	0.425	0.464	2.45	2.28	100.6	96.6
369.29	4.21	9.89	1.05	1.02	3.74	3.83	99.2	99.0
368.18	9.43	14.74	0.755	0.781	2.91	3.01	101.8	98.9
366.15	9.47	25.20	0.636	0.646	2.32	2.20	100.7	96.9
369.49	11.30	9.54	0.875	0.872	3.61	3.62	102.0	100.3
368.87	14.12	8.36	0.775	0.845	4.11	3.73	99.8	97.2
368.66	20.52	9.32	0.675	0.736	4.19	3.44	100.0	97.0
368.77	23.06	8.75	0.688	0.721	3.79	3.47	99.4	96.9
368.03	23.80	11.15	0.606	0.665	3.68	3.17	99.7	95.6
366.23	25.53	26.61	0.500	0.500	2.02	2.03	100.1	96.1
367.42	39.26	23.67	0.464	0.466	2.18	2.16	101.2	96.5
369.63	40.38	9.10	0.600	0.604	3.78	3.26	100.8	98.2
368.50	41.12	10.15	0.596	0.577	4.05	3.17	101.4	94.3
367.89	45.49	25.62	0.429	0.448	2.14	2.09	100.6	96.4
Standard deviation			—	5.2	—	9.5	—	3.4

Concentrations in wt. %

ane concentrations from about 7 to 27 wt. %. They thus covered substantially the same range as the measurements by Petrov et al. In Table 7 all measured results are compared with calculated data. Additionally, some results of the comparison are shown in Figure 10.

The differences between the calculated and the measured concentrations in the gas phase are significantly smaller than in the case of the comparison with the measurements of Petrov et al. For instance, the standard deviation of the calculated formaldehyde concentration ratio from the measured ratio is only 5.2%. In the case of the trioxane content of the gas phase, the standard deviation is 9.5% if all the measured values are included in the comparison, while it is 6.3% if the five measured points of maximum deviation are ignored. The calculated pressures are systematically below the measured values. One probable cause for this finding is that the feed solutions used in the measurements could not be degassed. The standard deviation of 3.4% is thus likely to be within the experimental error.

This comparison with these new experimental results consequently confirms that it is possible to extend the model for describing the vapor-liquid equilibrium for the binary mixture of formaldehyde and water to multicomponent mixtures with at least one additional chemically inert compound.

Extension of the Model to Multicomponent Mixtures with an Additional Chemical Reactive Component: The Ternary System Formaldehyde-Water-Methanol

Because formaldehyde reacts with methanol in a similar manner as it does with water, the ternary system of formaldehyde, water, and methanol is considered as an example. The conditions for phase equilibrium in this system are given by Eqs. 1, 2,

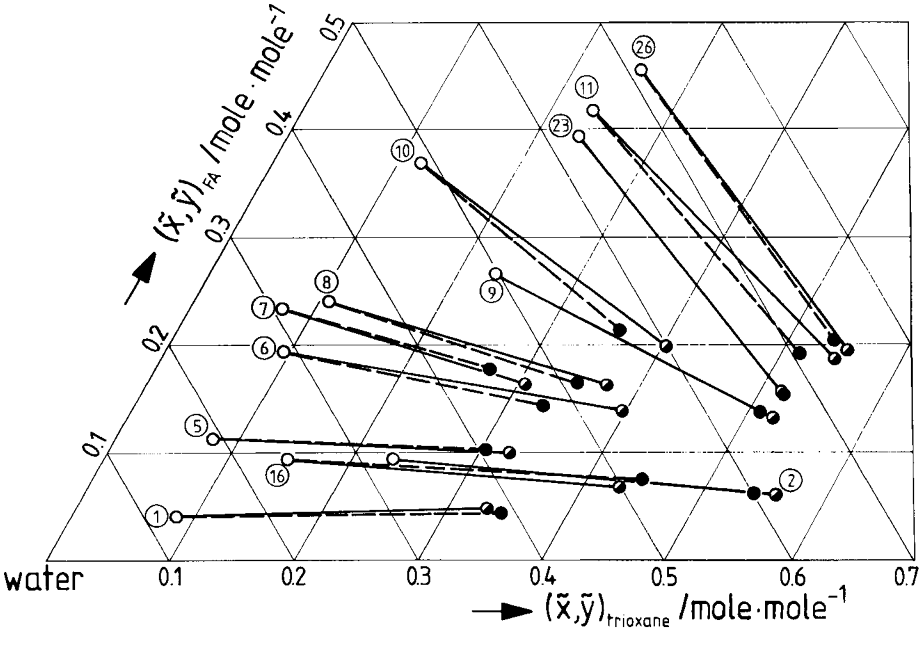


Figure 10. VLE in the ternary system formaldehyde-water-trioxane.

○ liquid phase; ◐ gaseous phase (exp.); ● gaseous phase (calc.).
Numbers in circles refer to lines in Table 7.

Table 8. Comparison between Measured and Calculated VLE in a Mixture of Formaldehyde, Water, and Methanol

Authors	Type of Measurement and No. of Exp. Points	Conc. in Liquid Phase mol %		Std. Dev. in			Mean Dev. in Calc. Boiling Temp. K
		$\bar{x}_{FA}$	$\bar{x}_{Me}$	P	$\bar{y}_{FA}$	$\bar{y}_{Me}$	
Green and Vener (1955)*	P = 101.3 kPa 30	2.3–43.3	1.4–94.3	1.9	18.3	16.6	0.50
Kogan and Ogorodnikov (1980a)	P = 101.3 kPa P = 26.7 kPa 15	5.2–23.5 4.9–22.3	5.0–79.4 10.0–79.9	4.4	9.4	7.8	0.96
Blazhin et al. (1976)	P = 101.3 kPa P = 26.7 kPa	9.6–25.5 14.7–15.2	4.9–79.4 13.7–71.4	4.7	14.2	7.3	1.10
Kogan and Ogorodnikov (1980b)	T = 333.15 K 27	2.7–49.9	2.8–89.0	1.7	4.9	6.3	0.36
	T = 343.15 K 29	4.1–50.0	3.3–88.4	1.4	9.0	7.4	0.30
	T = 353.15 K 26	3.8–50.7	3.1–83.0	1.5	11.5	9.8	0.37

Concentrations in wt. %

*From given numbers for the composition of the liquid phase and the pressure

3, 13, 14—physical equilibria—and Eqs. 4, 5, 6, 15, 16 and 17—chemical equilibria. Solving these equations by also taking into account the mass balances in the coexisting phases yields the distribution of the three components to the liquid and gaseous phases.

In addition to the data already reported while describing the model for the formaldehyde-water and formaldehyde-methanol systems, only some UNIFAC interaction parameters are required for these calculations: UNIFAC parameters for interactions between i = CH_3O— and j = H_2O, $CH_2(OH)_2$, —OH or CH_2O— were estimated by the corresponding parameters where i represents —CH_2O—:$A_{i,j} = A_{CH_2O,j}$; $A_{j,i} = A_{j,CH_2O}$.

UNIFAC parameters for interactions between methanol on one side and water, the OH-group, and the CH_2-group on the other side were taken as reported by Gmehling et al. (1982). In modeling the formaldehyde-methanol system the CH_2OH-group was considered to behave like methanol. Accepting this assumption also for interactions of CH_2OH with j = H_2O, $CH_2(OH)_2$, -OH or —CH_2— resulted in $A_{CH_2OH,j} = A_{CH_3OH,j}$ and $A_{j,CH_2OH} = A_{j,CH_3OH}$. The only unknown interactions are then those between methylene glycol [$CH_2(OH)_2$] and methanol, which are assumed to be the same as between water and methanol. All UNIFAC interaction parameters are given in Table 1c. As no parameters had to be fitted to experimental vapor-liquid equilibrium data for the ternary mixture, the model is completely predictive.

Comparison of calculated and measured VLE in the ternary system formaldehyde-water-methanol

Comparison with Data from the Literature. Measurements on the ternary system have been published by Green and Vener (1955), by Blazhin et al. (1976), and by Kogan and Orgorodnikov (1980a,b). Table 8 gives a comprehensive comparison of these measurements with calculated values; in the calculations the temperature and composition of the liquid phase were predetermined and the pressure and concentration in the gas phase were calculated (for a detailed comparison refer to the supplementary material).

Green and Vener carried out measurements at atmospheric pressure for formaldehyde and methanol concentrations of about 2–40 and 1.5–95 wt. %, respectively. The standard deviation of the calculated from the measured pressures is about 1.9%, with the calculated pressure being greater than the measured value for almost one-third of the data. The standard deviation of the calculated from the measured formaldehyde concentrations is slightly greater than 18% corresponding to an absolute value of 1.3 wt. %, with almost exactly half the calculated values being greater than the measured values. These deviations are largely determined by the results of four (out of 30) measured points at low formaldehyde concentrations, in which the deviations are from 30 to 50%. If these four points are neglected, the standard deviation drops to about 11%. Taking all measured values into account, the standard deviation of the methanol content is 16.6%, with the differences in the case of seven values being sometimes substantially greater than 10%. If these seven values are omitted from the error calculation, the deviation drops to only 6.6%. In the case of methanol, again, about half the calculated concentrations in the gas phase are greater than the measured values.

In 1976 Blazhin et al. reported the results of 25 experimental points taken at 26.7 and 101.3 kPa (200 and 760 mm Hg). The experimental results for the pressure are predicted by the model with a standard deviation of 4.7%—the standard deviations for the formaldehyde and methanol content in the gas phase are 14.2 and 7.3%, respectively.

Kogan and Ogorodnikov (1980a) investigated the same pressure range. The predicted numbers for the pressure and the gas phase composition agree well with the experimental results, standard deviations being 4.4% (pressure), 9.4% ($\bar{y}_{FA}$), and 7.8% ($\bar{y}_{ME}$). The model also reliably matches isothermal measurements by the same authors (1980b). For the three isotherms examined, namely 333.15, 343.15, and 353.15 K, the standard deviation as regards reproducing the pressure is 1.7, 1.4, and 1.5%, respectively, with approximately equal numbers of calculated values lying above and below the measured values. The standard deviations of the formaldehyde content in the gas phase are 4.9, 9.0 and 11.5%, with the calculated values almost

Table 9. Measured and Calculated VLE in the System Formaldehyde-Water-Methanol

Experimental Results, mol %										Calculated Results, mol %			
Temp. T/K	Press. P/kPa	Liquid		Vapor		Mass Balance*			$\frac{\text{Liquid}}{\text{Vapor}}$ kg/kg	Press. P/kPa	$\tilde{y}_{FA}$	$\tilde{y}_{Me}$	Boil. Pt. Temp., T K
		$\tilde{x}_{FA}$	$\tilde{x}_{Me}$	$\tilde{y}_{FA}$	$\tilde{y}_{Me}$	FA	Me	W					
362.78	77.3	10.34	3.20	9.75	9.48	−0.4	−1.2	0.9	4.6	76.8	10.08	10.35	362.93
363.41	79.6	10.31	3.41	9.87	10.68	−0.2	0.1	0.0	8.3	79.2	10.09	10.97	363.56
364.29	95.5	4.59	6.71	4.55	25.75	−0.2	1.8	−0.3	5.6	95.2	4.78	26.29	364.39
364.40	92.6	4.59	5.65	4.73	22.48	0.0	0.9	−0.2	3.5	92.3	4.99	22.95	364.48
364.20	89.1	13.08	7.08	11.02	18.95	0.8	12.0	−0.4	8.1	87.5	11.13	19.22	364.66
364.62	88.5	13.23	6.48	11.30	17.63	−0.2	1.4	0.2	4.7	87.6	11.42	17.61	364.87
364.39	84.6	19.55	9.07	14.67	18.94	−0.2	−1.9	0.6	3.9	87.5	14.33	19.85	363.53
363.48	81.7	19.68	8.94	14.67	19.04	−0.4	−1.8	0.7	4.0	84.1	14.29	19.60	363.00
362.81	101.7	18.12	18.92	11.09	37.43	−0.7	8.0	0.1	5.5	100.3	11.18	38.82	363.17
362.79	102.2	17.97	19.11	10.88	37.57	0.0	−0.7	0.5	6.2	100.8	11.05	39.22	363.16
342.91	104.1	9.95	80.10	2.19	92.91	−1.2	−0.12	4.0	9.4	104.9	2.14	92.98	342.72
342.99	31.9	22.02	3.85	14.31	8.55	−0.06	−0.18	0.0	11.1	31.9	12.72	9.19	343.01
344.65	55.0	17.49	25.65	8.77	49.23	−0.6	−0.9	−0.6	6.9	56.4	8.26	51.42	342.55
343.31	41.2	20.31	16.11	12.33	31.13	1.3	−1.3	−0.03	10.1	42.6	10.86	35.53	344.02
344.71	74.4	13.92	40.64	4.94	67.72	0.7	−0.8	1.1	5.3	74.6	5.00	68.41	344.65
342.38	32.1	32.35	8.80	16.89	14.73	0.7	2.4	−1.2	10.2	31.5	16.32	16.88	342.83
343.99	44.6	26.87	23.28	14.35	39.59	0.0	−0.7	0.6	10.1	46.4	12.98	43.31	343.04
342.76	54.3	23.70	30.22	8.81	52.22	0.2	−0.4	0.3	13.6	51.9	10.46	54.07	343.86
346.13	77.3	17.87	43.85	6.15	68.32	−0.14	−0.1	−0.35	5.1	78.4	6.40	69.49	345.79
342.61	31.2	44.25	45.76	22.87	21.76	0.10	0.3	−0.4	12.1	31.6	21.40	26.98	342.35
343.22	42.3	37.03	30.58	19.37	44.37	1.1	0.7	−3.1	9.7	44.5	17.16	50.28	342.05
344.10	50.6	32.71	35.86	15.01	53.74	0.5	−0.1	0.6	5.4	53.1	14.39	57.47	342.94
348.98	73.6	30.53	44.39	12.82	63.48	2.5	−0.6	−2.7	9.8	75.2	12.59	66.48	348.41
										Standard Deviation			
										2.6 ≙ 1.5 kPa	6.9 ≙ 0.9 mole %	8.5 ≙ 2.5 mole %	— 0.75 K

*Mass of component i in the feed not detected in the liquid or vapor phase (%).

always being lower than the measured values. The calculated concentrations of the methanol content in the gas phase are also mostly lower than the measured values, the standard deviations being 6.3, 7.4, and 9.8%.

Comparison with measurements of this study

A number of vapor-liquid equilibrium measurements were carried out on the formaldehyde-water-methanol system with the same thin film evaporator that was used for the experiments on the formaldehyde-water-trioxane system. The formaldehyde content was determined by the sodium sulfite method and the water/methanol ratio by gas chromatography. The uncertainty in the determination is probably about 0.15 kPa in respect to pressure and about 0.15 K in respect to temperature. The error in the formaldehyde concentrations is expected not to exceed about 2%. From calibraton measurements on the gas chromatograph, the relative error in determining the methanol concentration was estimated at about 3%. The temperature range covered by these measurements is from about 343 to 365 K and the pressure ranges from 30 to 104 kPa. The liquid phase concentrations are from 4.5 to 44 mol % formaldehyde and from 3 to 80 mol % methanol. Table 9 gives the experimental results together with the comparison with predicated data. Some typical results are also shown in Figure 11. The standard deviation for 23 experimental points is 2.6% in respect to pressure and 6.9 and 8.5% in

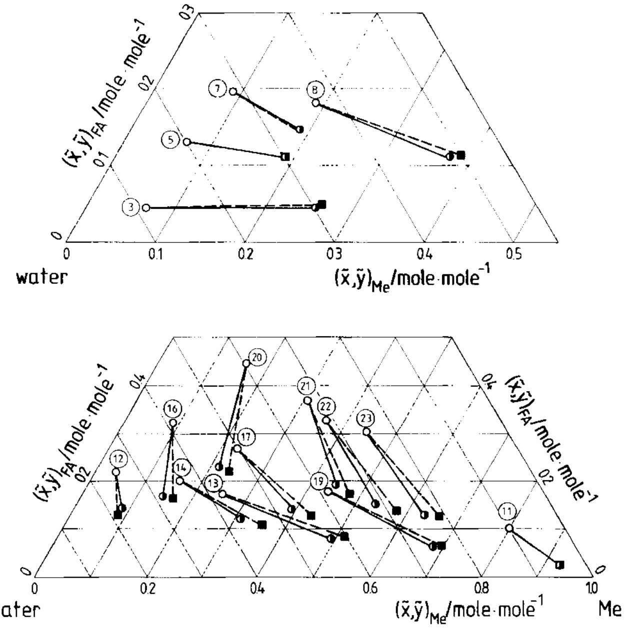


Figure 11. VLE in the ternary system formaldehyde-water-methanol.

○ liquid phase; ○ gaseous phase (exp.); ■ gaseous phase (calc.). Numbers in circles refer to lines in Table 9.

respect to the formaldehyde and methanol concentration in the gas phase.

Summary

Comparisons of calculated and measured vapor-liquid equilibria in the binary systems formaldehyde-water and formaldehyde-methanol proved that the physicochemical model presented here is able to accurately correlate phase behavior in chemically reacting systems. Similar comparisons for the ternary systems formaldehyde-water-trioxane and formaldehyde-water-methanol confirmed that extensions of that model to multicomponent mixtures containing additional chemically inert or chemically reactive components are suitable to adequately predict the vapor-liquid equilibrium in such complex systems.

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Notation

a_i, b_i, c_i = constants in Antoine equation for component i
$A_{i,j}$ = UNIFAC parameter for interactions between groups i and j
f = fugacity
D_k = deviation between experimental and calculated numbers for d at a certain data point $k[D_k = (d_{k,\mathrm{exp}} - d_{k,\mathrm{cal}})/(d_{k,\mathrm{exp}})]$
K_i, K_i^* = chemical equilibrium constant for formation of polyoxymethylene with i CH_2O— segments
$K_{m,i}; K_{m,i}^*$ = chemical equilibrium constant for formation of hemiformal with i CH_2O— segments
K_x = pseudochemical equilibrium constant
N = number of experimental points
P = pressure
p^{ϕ} = standard pressure, 101.325 kPa
p_i^s = vapor pressure of component i
q = UNIFAC surface parameter
r = UNIFAC size parameter
s = standard deviation $\{s = 100[1/(N-1)\ \Sigma_{k-1}^{N}\ D_k^2]^{1/2}\}$
T = absolute temperature, K
x = mole fraction in liquid phase
y = mole fraction in gaseous phase
z = average deviation $[z = (100/N)\ \Sigma_{i-1}^{N}\ D_k]$
γ_j = activity coefficient of component j

Subscripts

calc = calculated
exp = experimental
FA = formaldehyde
HF = hemiformal
i = component or group
j = component or group
Me = methanol
MG = methylene glycol
max = maximum
m, n = hemiformal with n CH_2O— segments
n = polyoxymethylene with n CH_2O— segments
W = water

Superscripts

∞ = infinite
$\sim$ = overall (stoichiometric)
I = liquid phase
II = gaseous phase

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