Vapor–Liquid Equilibrium of Aqueous Solutions of Formaldehyde and Methanol

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A thermodynamic model for phase and chemical equilibrium in formaldehyde–water mixtures was extended to describe vapor–liquid and chemical equilibrium in the binary formaldehyde–methanol system and in the ternary formaldehyde–water–methanol system. Ternary mixtures were extended using new experimental vapor–liquid equilibrium data for the influence of especially small amounts of methanol on the volatility (of small amounts) of formaldehyde in aqueous solutions. New experimental data for the range 333 to 383 K are reported. Some model parameters were fitted to ternary phase equilibrium data, because of cross-reactions between poly(oxymethylene) glycols and poly(oxymethylene) hemiformals, and strong influence of interactions between those species on the phase equilibrium of the ternary mixture. The new model presents a reliable method for calculating vapor–liquid equilibrium and the conversion of formaldehyde to reaction products [poly(oxymethylene) glycols and poly(oxymethylene) hemiformals] over the whole range of temperature and composition where reliable experimental data are available.

Introduction

Formaldehyde is a very important industrial chemical. It is an intermediate present in several industrial processes (such as trioxane production, polymers and adhesive synthesis, etc.). Modeling of thermodynamic properties of formaldehyde solutions has been a research topic of several research groups for many years (such as Blazhin et al., 1976; Kogan and Ogorodnikov, 1980a,b; Brandani et al., 1991a,b, 1992, 1998; Maurer, 1986; Hasse et al., 1990; Albert et al., 1996, 1999; Balashov et al., 1996). Despite immense progress, much work remains to provide a model for fulfilling the requirements of process simulation. Because formaldehyde is highly reactive, it is not possible to store or process formaldehyde as a pure substance. It is usually stabilized in binary solutions with water. Methanol is sometimes added to reduce the amount of water in a specific process or to enhance the solubility of formaldehyde in an aqueous phase. Furthermore, methanol is also formed in a chemical reaction in aqueous solutions of formaldehyde. Therefore, it is often necessary to consider ternary formaldehyde–water–methanol mixtures. In most cases, addition of methanol results in a lowering of the volatility of formaldehyde. However, at low temperatures addition of very small amounts of methanol to a binary formaldehyde–water solution may result in a considerable increase in the volatility of formaldehyde (Hasse and Maurer, 1991).

Mixtures of formaldehyde with water or methanol are not binary solutions in the usual sense, since formaldehyde reacts with both of them to form a variety of reaction products. Reactions with water lead to methylene glycol ($HOCH_2OH$; here also MG) and poly(oxymethylene) glycols ($HO(CH_2O)_iH$, $i > 1$; here also, MG_i), and reactions with methanol lead to hemiformal ($HOCH_2OCH_3$; here also HF) and poly(oxymethylene) hemiformals ($HO(CH_2O)_iCH_3$, $i > 1$; here also HF_i):

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \qquad (I)$$

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

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

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

These chemical reactions have an essential influence on the properties of formaldehyde-containing mixtures and they have to be explicitly taken into account in the thermodynamic models for phase equilibrium and caloric properties. A physicochemical model successfully used in the description of thermodynamic properties for this kind of system was given before (Maurer, 1986). The performance of that model has been continuously improved and its range of application extended based on new experimental data for vapor−liquid equilibrium (Hasse et al., 1990; Hasse and Maurer, 1991; Albert et al., 1996) as well as for thermal properties (Liu et al., 1992). Knowledge of the chemical equilibrium reaction constants in the liquid phase has also been extended by NMR spectroscopy (Kogan, 1979a; Hahnenstein et al., 1994a, 1995; Balashov et al., 1996). Recently, new experimental data for vapor−liquid equilibrium and for chemical-reaction equilibrium in the liquid phase have been used to update and extend the model for the binary system formaldehyde−water (Albert et al., 1999). That model update is able to give accurate values for phase equilibrium properties as well as for the oligomer distribution in the liquid phase of binary formaldehyde−water mixtures.

Extension of this model to formaldehyde−methanol mixtures is similar to that developed for formaldehyde−water mixtures. Since the model contains only binary interaction parameters, it can also be straightforwardly extended to describe ternary formaldehyde−water−methanol mixtures without further modification. However, some additional difficulties appear in this extension, as several species appear simultaneously only in the ternary mixtures; for example, methylene glycol or poly(oxymethylene) glycols will be present simultaneously with methanol, hemiformal, or poly(oxymethylene) hemiformals only in ternary (and higher) mixtures containing water, methanol, and formaldehyde. Therefore, some model parameters (that is, interaction parameters) cannot be obtained from binary experimental data alone, but must be estimated or determined from experimental data for the ternary mixture. In addition, interchange between poly(oxymethylene) glycol and poly(oxymethylene) hemiformal chains must be considered through free (that is, molecular) formaldehyde (cf. reactions I and III). Because in binary solutions of formaldehyde with either water or methanol, formaldehyde is predominantly present as MG/MG_i and HF/HF_i, respectively, reactions I and III have only a small effect in the binary formaldehyde−water and formaldehyde−methanol systems. However, they have an essential influence on the properties of the ternary system due to this interchange effect. To avoid difficulties when considering very small values for the concentration of free formaldehyde, a linear combination of reactions I and III can be used to replace either reaction I or III:

$$HOCH_2OH + CH_3OH \rightleftharpoons HOCH_2OCH_3 + H_2O. \quad \text{(V)}$$

In the present work, the revised model for the thermodynamic properties of the binary formaldehyde−water system (Albert et al., 1999) is extended to the binary formaldehyde−methanol system and the ternary formaldehyde−water−methanol system. Extension to the formaldehyde−methanol system was carried out following a procedure similar to that described for the formaldehyde-water system: vapor−liquid and chemical equilibrium data were taken from the literature (Blazhin et al., 1976; Kogan 1979b; Kogan and Ogorodnikov, 1980a,b; Maurer, 1986; Hasse and Maurer, 1991; Hahnenstein et al., 1994a,1995; Balashov et al., 1996) and correlated simultaneously. The revised model gives a reliable representation of the experimental data from phase-equilibrium measurements as well as from spectroscopic investigations (that is, for the concentration of poly(oxymethylene) hemiformals in the liquid phase) over the entire composition and temperature ranges where reliable experimental data are available.

Extension to the ternary formaldehyde−water−methanol system is based on data in the literature as well as on new experimental data for vapor−liquid equilibrium. While the data from the literature cover a wide range of methanol composition at higher formaldehyde concentrations, the new ex− perimental investigations focus on the influence of small methanol concentrations on the volatility of formaldehyde, particularly at temperatures between about 333 and 383 K, particularly in the region where the partition coefficient of formaldehyde (that is, the ratio of the overall mol fraction of formaldehyde in the vapor to that in the liquid: $\tilde{y}_{FA}/\tilde{x}_{FA}$) goes through a maximum with increasing methanol concentration. The new experimental data extend the available data to concentration ranges that are particularly important from an environmental point of view (low formaldehyde as well as low methanol concentration in an aqueous solution near ambient temperature). The updated model gives a correct description of vapor−liquid equilibrium for the formaldehyde−water−methanol system over the whole region where reliable experimental data are available for comparison.

Experimental Section

There is a large number of publications on experimental investigations of the vapor−liquid equilibrium of formaldehyde-containing mixtures. However, only a small number of these sources provides reliable data (for a review, cf. Blazhin et al., 1976; Kogan and Ogorodnikov, 1980a,b; Maurer, 1986; Hasse and Maurer, 1991; Albert et al., 1996, 1999). As shown previously (Hasse, 1990; Hasse and Maurer, 1991), a very small amount of methanol has a remarkable influence on the volatility of formaldehyde, particularly at low temperatures. But the experimental evidence for that effect is scarce, as only a few reliable experimental data sets are available (for about 293 and 313 K). While predictions of the former model revealed this influence, quantitative agreement was not achieved and—as only a very limited amount of reliable experimental data were available—no effort has been undertaken to fine-tune the model. Therefore, the experiments of the present work were dedicated to investigate the influence of small amounts of methanol on the volatility of formaldehyde in aqueous solutions under conditions where that effect is important, that is, at low concentrations of formaldehyde and temperatures between about 333 and 383 K.

The phase-equilibrium apparatus for investigating the vapor−liquid equilibrium has been described previously (Albert et al., 1996). It is a thin-film evaporator in which a rotating coil spreads the liquid feed on the inner surface of a tube, surrounded by a heating jacket. The liquid partially evaporates. The coexisting phases are separated and collected in vials. Experiments can be carried out at small evaporation ratios and high residence times, so that chemical equilibrium in the liquid phase leaving the apparatus is achieved. Stainless steel was used for the thin-film evaporator; it can be used at temperatures from about 323 to about 423 K and at pressures up to about 1 MPa.

The temperature of the coexisting phases is measured by platinum-resistance thermometry with an uncertainty below ± 0.1 K. The pressure is measured with differential pressure transducers (WIKA, Klingenberg, Germany). The experimental uncertainty is smaller than ± 0.5 kPa and ± 0.2 kPa at pressures above and below ambient pressure, respectively.

Either gas chromatography (GC) or wet chemistry was used for analyzing the composition of the coexisting phases. Commercial GC equipment was used (Hewlett-Packard: GC: model HP-5890A; injector: model HP-7673; column packing: Poropack T). The strong interactions between formaldehyde on one side and water or methanol on the other side result in some difficulties in gas-chromatographic analysis. For example, the peaks of formaldehyde were extremely broad at very high methanol concentrations. They could not be correctly integrated. Therefore, those samples were diluted with known amounts of water before a GC analysis. On the other hand, the gas chromatographic resolution of the formaldehyde peaks was not sufficient at formaldehyde concentrations below about 0.01 $g \cdot g^{-1}$. This problem arose especially with samples that had to be diluted. In these cases, the sodium-sulfite method (Walker, 1964) was used to determine the formaldehyde concentration, while the concentration of methanol was determined by gas chromatography. Relative errors, estimated on the basis of carefully performed calibrations, are about 2% in both procedures. No systematic deviations were obtained between results from the different methods.

Binary formaldehyde−water solutions were prepared by dissolving paraformaldehyde (Merck, purity higher than 95%) in bidistilled water at elevated temperature; any remaining solid residue was removed by filtration (Hasse, 1990). The solutions were used for preparing methanolic mixtures by further dilution with water and/or methanol (Merck, purity higher than 99.8%).

Vapor−liquid equilibrium in the formaldehyde−water−methanol system was investigated experimentally at about 333, 363 and 383 K. The overall concentration of formaldehyde in the feed solutions was $\tilde{\xi}_{FA} = 0.01$ $g \cdot g^{-1}$ at 333, 363 and 383 K; $\tilde{\xi}_{FA} = 0.05$ $g \cdot g^{-1}$ at 333 K; and $\tilde{\xi}_{FA} = 0.15$ $g \cdot g^{-1}$ at 333 and 363 K. The concentration of methanol in the feed ranged from about 0.02 $mol \cdot mol^{-1}$ to 0.70 $mol \cdot mol^{-1}$.

Results of the vapor−liquid equilibrium measurements are given in Tables 1 to 3. Some typical results are shown in Figures 1 and 2. The new experimental results confirm that the partition coefficient of formaldehyde goes through a maximum when small amounts of methanol are added to an aqueous solution of formaldehyde. The maximum increases with decreasing temperature and decreasing formaldehyde concentration in the liquid phase. It is no longer observed at temperatures above about 383 K and liquid-phase formaldehyde concentrations above about 0.15 $g \cdot g^{-1}$. The experimental results of the present work show strongest enhancement for the partition coefficient of formaldehyde at both the lowest temperature and the lowest formaldehyde concentration (that is, at 333 K and $\tilde{\xi}_{FA} \approx 0.01$ $g \cdot g^{-1}$: $(\tilde{y}_{FA}/\tilde{x}_{FA})_{max,\ with\ methanol} = 1.0$, whereas $(\tilde{y}_{FA}/\tilde{y}_{FA})_{without\ methanol} = 0.83$). That enhancement decreases with increasing formaldehyde concentration. For example, at 333 K, the increase is reduced from about 20% at $\tilde{\xi}_{FA} \approx 0.01$ $g \cdot g^{-1}$ to about 12% and about 9% at $\tilde{\xi}_{FA} \approx 0.05$ $g \cdot g^{-1}$ and $\tilde{\xi}_{FA} \approx 0.15$ $g \cdot g^{-1}$, respectively. The enhancement decreases with increasing temperature. For example, at 363 K the maximum enhancement is 9% at $\tilde{\xi}_{FA} \approx 0.01$ $g \cdot g^{-1}$ and less than 1% at $\tilde{\xi}_{FA} \approx 0.15$ $g \cdot g^{-1}$. In previous experimental work for lower temperatures (Hasse and Maurer, 1991), the addition of small amounts of methanol to an aqueous solution of $\tilde{\xi}_{FA} \approx 0.15$ $g \cdot g^{-1}$ increased the formaldehyde partition coefficient by up to 60% at 293 K and up to 35% at 313 K. The maximum of the formaldehyde partition coefficient is difficult to verify experimentally at temperatures above about 320 K because it appears at very small methanol concentrations, that is, in a region hardly accessible experimentally. Therefore, most published data confirm the finding that methanol reduces the volatility of formaldehyde, but that statement is only valid for higher methanol concentrations, at higher formaldehyde concentrations, as well as at higher temperatures.

Model

The model used to correlate the experimental results considers chemical reactions in both phases as well as differences in interactions between all species in the liquid phase. The vapor phase is considered to be an ideal mixture of formaldehyde, water, methanol, methylene glycol, and hemiformal. The main features of that model have been described before (Maurer, 1986). The model has been continuously updated and extended as more reliable experimental data became available (cf. Hasse et al., 1990; Hasse and Maurer, 1991; Hahnenstein et al., 1994b; Albert et al., 1996, 1999). Because reaction and transport kinetics become important in the design of separation equipment at lower temperatures, the aim of most recent work was to give a reliable representation of the distribution of formaldehyde oligomers in aqueous solutions.

The oligomer distribution can be studied with NMR spectroscopy. Experimental investigations by that technique provided essential progress in our knowledge of chemical-reaction equilibrium in aqueous and methanolic formaldehyde solutions (Kogan, 1979a; Le Botlan et al., 1983, Hahnenstein et al., 1994a; Balashov et al., 1996). However, combining chemical- and phase-equilibrium properties in a thermodynamic model is not straightforward, since spectroscopic data are re-

Table 1. New Experimental Results for the Vapor–Liqud Equilibrium of the Formaldehyde–Water–Methanol System at 333 K

T/K	$\tilde{x}_{FA}$	$\tilde{x}_{ME}$	$\tilde{y}_{FA}$			$\tilde{y}_{ME}$			p		
			Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	Δp
	$\mathrm{mol\cdot mol^{-1}}$		$\mathrm{mol\cdot mol^{-1}}$		%	$\mathrm{mol\cdot mol^{-1}}$		%	kPa		%
333.1	0.0057	0.0084	0.0052	0.0052	−0.19	0.0583	0.0695	19.18	20.5	21.2	3.32
333.1	0.0059	0.0061	0.0051	0.0052	3.01	0.0453	0.0512	13.02	20.2	20.8	2.99
333.1	0.0058	0.0173	0.0056	0.0054	−2.43	0.1155	0.1322	14.44	21.7	22.5	3.95
333.1	0.0059	0.0145	0.0055	0.0055	−0.47	0.0974	0.1135	16.57	21.2	22.1	4.40
333.2	0.0061	0.0286	0.0061	0.0057	−5.85	0.1823	0.1985	8.89	23.3	24.2	3.96
333.2	0.0060	0.0297	0.0059	0.0056	−4.90	0.1816	0.2050	12.91	23.5	24.4	4.21
333.2	0.0062	0.0547	0.0056	0.0054	−3.39	0.2915	0.3152	8.10	26.5	27.7	4.66
333.1	0.0068	0.1312	0.0043	0.0045	3.56	0.5055	0.5051	−0.08	34.8	35.7	2.71
333.1	0.0074	0.2029	0.0033	0.0037	13.38	0.6059	0.6003	−0.92	41.1	41.6	1.37
333.1	0.0082	0.4130	0.0021	0.0024	15.85	0.7765	0.7523	−3.11	53.5	54.5	1.99
333.1	0.0082	0.4144	0.0021	0.0024	15.82	0.7573	0.7531	−0.55	53.5	54.6	2.08
333.1	0.0089	0.6398	0.0016	0.0018	14.44	0.8501	0.8576	0.89	63.4	66.1	4.38
333.1	0.0317	0.0111	0.0246	0.0265	7.78	0.0549	0.0706	28.65	20.2	21.1	4.32
333.2	0.0312	0.0138	0.0250	0.0264	5.83	0.0648	0.0866	33.62	20.5	21.4	4.67
333.2	0.0312	0.0297	0.0261	0.0270	3.66	0.1371	0.1705	24.36	22.1	23.3	5.33
333.1	0.0312	0.0319	0.0264	0.0269	2.14	0.1482	0.1808	21.98	22.2	23.5	5.77
333.1	0.0317	0.0601	0.0246	0.0260	5.66	0.2612	0.2934	12.34	25.0	26.7	6.69
333.2	0.0323	0.0581	0.0257	0.0267	4.08	0.2531	0.2855	12.78	25.0	26.5	6.20
333.1	0.0341	0.1373	0.0211	0.0217	3.09	0.4561	0.4793	5.09	32.9	34.2	3.96
333.2	0.0355	0.2077	0.0175	0.0179	2.29	0.5698	0.5774	1.34	39.5	39.8	0.83
333.1	0.0348	0.2092	0.0171	0.0175	2.01	0.5676	0.5799	2.16	39.5	40.0	1.07
333.1	0.0369	0.3880	0.0122	0.0118	−2.94	0.7224	0.7254	0.41	49.8	51.3	3.19
333.1	0.0377	0.3792	0.0121	0.0123	1.88	0.7291	0.7195	−1.33	49.4	50.7	2.50
333.1	0.0433	0.6155	0.0099	0.0097	−1.67	0.8662	0.8441	−2.56	61.5	63.3	2.89
333.1	0.0436	0.6343	0.0098	0.0096	−2.09	0.8499	0.8528	0.35	61.5	64.2	4.39
333.1	0.0976	0.0324	0.0694	0.0680	−2.09	0.1017	0.1281	25.99	20.6	21.8	5.82
333.1	0.1001	0.0570	0.0712	0.0695	−2.37	0.1700	0.2074	21.95	22.2	23.6	6.33
333.2	0.1013	0.0550	0.0710	0.0702	−1.07	0.1617	0.2004	23.98	22.1	23.5	6.68
333.1	0.1053	0.1345	0.0654	0.0643	−1.65	0.3598	0.3916	8.85	27.7	29.5	6.59
333.2	0.1103	0.2147	0.0540	0.0557	3.25	0.5078	0.5160	1.62	33.7	35.2	4.40

lated to compositions rather than to activities. Because reaction and transport kinetics are predominantly written with concentrations (instead of activities), in a previous investigation the species concentrations were calculated using chemical-reaction equilibrium constants where activities were replaced by concentrations, whereas the phase-equilibrium calculations were performed using activities (Albert et al., 1996). Because this approximation resulted in some inconsistencies, it was abandoned in more recent work (Albert et al., 1999).

The model for the formaldehyde–water system was described recently (Albert et al., 1999). Extension to the ternary formaldehyde–water–methanol system follows the main idea described before (Maurer, 1986). Therefore, only the most essential features are repeated here. The vapor phase is considered to be a mixture of ideal gases: formaldehyde (FA), water (W), methylene glycol (MG), methanol (ME), and hemiformal (HF). Real-gas corrections for that mixture as well as the presence of poly(oxymethylene) glycols (MG_i) and poly(oxymethylene) hemiformals (HF_i) are neglected. These assumptions are justified as both the total pressure and the vapor pressures of MG_i and HF_i are small. However, the condition of chemical-reaction equilibrium is considered. The liquid phase is considered to be a mixture of the species in the vapor phase as well as the MG_i and HF. The physical interactions between all species in the liquid phase are described using the UNIFAC group-contribution method (Fredenslund et al., 1977). The influence of pressure on the properties of the liquid phase is neglected. The oligomer distribution in the liquid phase follows from mass balances, assuming chemical reaction equilibrium:

$$\tilde{x}_{FA} = s\cdot\left[x_{FA} + x_{MG} + \sum_{i=2}^{\infty}\left(i\cdot x_{MG_i}\right) + x_{HF} + \sum_{i=2}^{\infty}\left(i\cdot x_{HF_i}\right)\right] \tag{1}$$

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

$$\tilde{x}_{ME} = s\cdot\left(x_{ME} + x_{HF} + \sum_{i=2}^{\infty} x_{HF_i}\right) \tag{3}$$

$$s = \left(1 + x_{MG} + \sum_{i=2}^{\infty}\left(i\cdot x_{MG_i}\right) + x_{HF} + \sum_{i=2}^{\infty}\left(i\cdot x_{HF_i}\right)\right)^{-1}. \tag{4}$$

Equilibrium constants for the formation of methylene glycol and hemiformal in the liquid phase $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$ are calculated from equilibrium constants for those reactions

Table 2. New Experimental Results for the Vapor–Liqud Equilibrium of the Formaldehyde–Water–Methanol System at 363 K

			$\tilde{y}_{FA}$			$\tilde{y}_{ME}$			p		
$\frac{T}{\text{K}}$	$\tilde{x}_{FA}$	$\tilde{x}_{ME}$	Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	Δp
	$\text{mol}\cdot\text{mol}^{-1}$		$\text{mol}\cdot\text{mol}^{-1}$		%	$\text{mol}\cdot\text{mol}^{-1}$		%	kPa		%
363.2	0.0058	0.0098	0.0082	0.0077	−5.30	0.0678	0.0691	1.90	74.7	74.8	0.06
363.2	0.0058	0.0113	0.0083	0.0077	−7.22	0.0734	0.0789	7.38	75.4	75.6	0.21
363.1	0.0061	0.0270	0.0078	0.0077	−1.45	0.1598	0.1678	4.97	81.9	82.1	0.33
363.1	0.0060	0.0278	0.0079	0.0075	−4.60	0.1656	0.1722	3.96	82.1	82.3	0.23
363.1	0.0062	0.0542	0.0066	0.0069	4.24	0.2762	0.2831	2.51	92.9	93.0	0.03
363.1	0.0063	0.0539	0.0067	0.0070	4.76	0.2756	0.2819	2.29	92.9	92.9	0.00
363.1	0.0068	0.1082	0.0058	0.0058	1.35	0.4327	0.4275	−1.21	110.9	110.7	−0.16
363.1	0.0068	0.1095	0.0056	0.0058	3.25	0.4264	0.4302	0.89	111.2	111.1	−0.06
363.1	0.0075	0.2053	0.0041	0.0045	8.44	0.5663	0.5693	0.53	137.2	135.7	−1.15
363.1	0.0076	0.2023	0.0042	0.0046	8.36	0.5711	0.5659	−0.92	137.0	135.1	−1.36
363.1	0.0090	0.4923	0.0025	0.0029	13.79	0.7730	0.7666	−0.84	184.0	184.8	0.40
363.2	0.0089	0.5126	0.0024	0.0028	13.87	0.7834	0.7768	−0.84	186.9	188.4	0.78
363.1	0.0978	0.0172	0.1024	0.0998	−2.60	0.0572	0.0584	2.02	75.2	74.6	−0.70
363.1	0.0957	0.0180	0.1000	0.0980	−1.94	0.0592	0.0616	4.12	75.1	74.7	−0.54
363.2	0.1007	0.0340	0.1028	0.0997	−3.08	0.1080	0.1105	2.30	78.7	78.0	−0.98
363.2	0.0996	0.0341	0.1030	0.0988	−4.09	0.1082	0.1114	2.96	78.7	78.0	−0.87
363.2	0.1026	0.0677	0.0951	0.0947	−0.41	0.1991	0.2048	2.84	85.7	85.0	−0.74
363.2	0.1027	0.0692	0.0952	0.0945	−0.74	0.2021	0.2087	3.24	86.1	85.4	−0.87
363.2	0.1073	0.1435	0.0806	0.0810	0.54	0.3611	0.3692	2.23	102.9	101.6	−1.32
363.1	0.1075	0.1410	0.0809	0.0817	1.09	0.3558	0.3642	2.38	102.1	100.7	−1.36
363.1	0.1117	0.2085	0.0687	0.0708	3.05	0.4646	0.4706	1.29	115.5	115.0	−0.39
363.2	0.1125	0.2078	0.0712	0.0715	0.33	0.4658	0.4688	0.65	115.5	114.9	−0.49
363.2	0.1292	0.3955	0.0541	0.0553	2.17	0.6564	0.6587	0.34	148.6	148.8	0.11
363.2	0.1259	0.4060	0.0515	0.0528	2.56	0.6525	0.6689	2.50	151.4	151.5	0.11

in the vapor phase $K_{MG,\text{gas}}$ and $K_{HF,\text{gas}}$:

$$K_{MG,\text{gas}} = \frac{y_{MG}}{y_{FA}\cdot y_W}\cdot\frac{p^{\ominus}}{p} \tag{5}$$

$$K_{MG,\text{liq}} = K_{MG,\text{gas}}\cdot\frac{p^s_{FA}\cdot p^s_W}{p^s_{MG}\cdot p^{\ominus}} \tag{5a}$$

$$K_{MG,\text{liq}} = \frac{x_{MG}}{x_{FA}\cdot x_W}\cdot\frac{\gamma_{MG}}{\gamma_{FA}\cdot\gamma_W} \tag{5b}$$

and

$$K_{HF,\text{gas}} = \frac{y_{HF}}{y_{FA}\cdot y_{ME}}\cdot\frac{p^{\ominus}}{p} \tag{6}$$

$$K_{HF,\text{liq}} = K_{HF,\text{gas}}\cdot\frac{p^s_{FA}\cdot p^s_{ME}}{p^s_{HF}\cdot p^{\ominus}} \tag{6a}$$

$$K_{HF,\text{liq}} = \frac{x_{HF}}{x_{FA}\cdot x_{ME}}\cdot\frac{\gamma_{HF}}{\gamma_{FA}\cdot\gamma_{ME}}. \tag{6b}$$

Table 3. New Experimental Results for the Vapor–Liqud Equilibrium of the Formaldehyde–Water–Methanol System at 383 K

			$\tilde{y}_{FA}$			$\tilde{y}_{ME}$			p		
$\frac{T}{\text{K}}$	$\tilde{x}_{FA}$	$\tilde{x}_{ME}$	Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	$\Delta\tilde{y}$	Exp.	Cal.	Δp
	$\text{mol}\cdot\text{mol}^{-1}$		$\text{mol}\cdot\text{mol}^{-1}$		%	$\text{mol}\cdot\text{mol}^{-1}$		%	kPa		%
383.1	0.0059	0.0099	0.0105	0.0101	−4.17	0.0648	0.0644	−0.66	152.6	152.2	−0.30
383.2	0.0060	0.0107	0.0105	0.0102	−2.58	0.0687	0.0693	0.83	154.0	153.4	−0.40
383.1	0.0060	0.0277	0.0093	0.0091	−2.15	0.1576	0.1602	1.63	167.7	166.6	−0.63
383.2	0.0060	0.0247	0.0097	0.0094	−3.37	0.1441	0.1453	0.83	165.6	164.3	−0.76
383.1	0.0063	0.0475	0.0090	0.0085	−5.64	0.2415	0.2426	0.44	182.8	181.3	−0.86
383.1	0.0063	0.0548	0.0085	0.0082	−4.00	0.2652	0.2686	1.29	187.9	186.3	−0.86
383.1	0.0065	0.1078	0.0067	0.0063	−6.18	0.4028	0.4082	1.35	221.0	219.6	−0.66
383.1	0.0073	0.1984	0.0047	0.0050	5.41	0.5394	0.5431	0.68	264.8	263.3	−0.59
383.2	0.0072	0.2074	0.0044	0.0048	7.97	0.5473	0.5530	1.05	268.9	267.4	−0.57
383.1	0.0103	0.4157	0.0041	0.0043	3.62	0.7004	0.7092	1.26	332.4	334.2	0.56
383.1	0.0101	0.4269	0.0038	0.0041	7.04	0.7081	0.7158	1.08	336.1	337.8	0.49

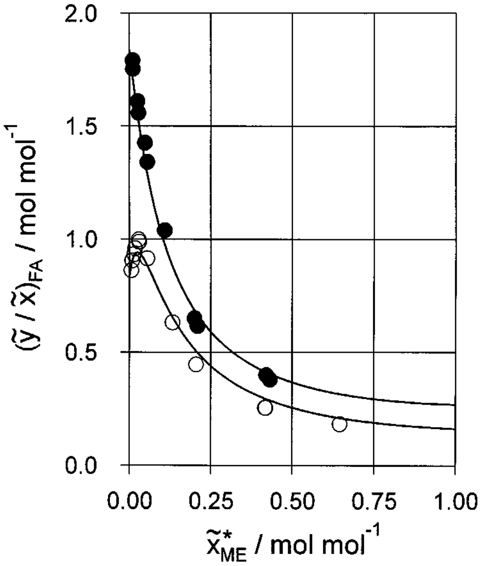

Figure 1. Formaldehyde–water–methanol.

Partition coefficient of formaldehyde at 333 and 383 K and $\tilde{\xi}_{FA} = 0.01$ g·g^{-1}; ○, ●, exp. (333 K, 383 K), this work; —, calc.

In former work, chemical-reaction equilibrium constants $K_{MG,\mathrm{gas}}$ and $K_{HF,\mathrm{gas}}$ were determined from experimental results for the density of the vapor phase in the binary formaldehyde–water and formaldehyde–methanol systems, as reported, for example, by Kogan (1979b). $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$ are of minor importance as long as only the binary formaldehyde–water and formaldehyde-methanol systems are considered. In such binaries, the numbers for the reaction equilibrium constants $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$ determine the concentration of molecular formaldehyde in the liquid phase. Because that concentration is always very small, numerical values for $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$ have no significant influence on vapor-liquid equilibrium. However, $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$ are very important in ternary liquid mixtures of formaldehyde, water, and methanol, as they describe the transition from the MG_i to the HF_i and vice versa.

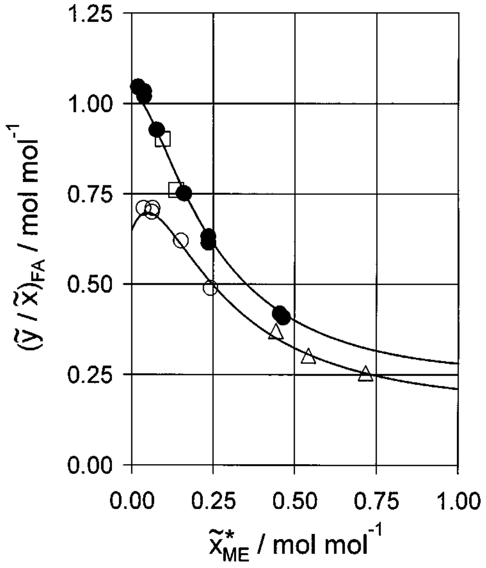

Figure 2. Formaldehyde–water–methanol.

Partition coefficient of formaldehyde at 333 and 363 K and $\tilde{\xi}_{FA} = 0.15$ g·g^{-1}; ○, ●, exp. (333 K, 363 K) this work; △, exp. (333 K), Kogan and Ogorodnikov (1980b); □, exp. (363 K), Blazhin et al. (1976); —, calc.

The model not only requires numerical values for chemical equilibrium constants $K_{MG,\mathrm{gas}}$, $K_{HF,\mathrm{gas}}$, $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$, but also for K_{MG_i} and K_{HF_i} $(i \geq 2)$ in the liquid phase (cf. chemical reactions II and IV). Correlation of the experimental data revealed that, for formation of the MG_i, a distinction was necessary between $i = 2$ and $i > 2$ (that is, the formation of the MG_i, with two and more formaldehyde groups). However, such a distinction was not necessary for formation of the HF_i. Therefore, three more chemical equilibrium constants are used in the model (besides $K_{MG,\mathrm{gas}}$, $K_{HF,\mathrm{gas}}$, $K_{MG,\mathrm{liq}}$ and $K_{HF,\mathrm{liq}}$):

$$K_{MG_2} = \frac{x_{MG_2}\cdot x_W}{x_{MG}\cdot x_{MG}}\cdot\frac{\gamma_{MG_2}\cdot\gamma_W}{\gamma_{MG}\cdot\gamma_{MG}} \qquad (8)$$

$$K_{MG_i} = \frac{x_{MG_i}\cdot x_W}{x_{MG_{i-1}}\cdot x_{MG}}\cdot\frac{\gamma_{MG_i}\cdot\gamma_W}{\gamma_{MG_{i-1}}\cdot\gamma_{MG}} \qquad i>2 \qquad (9)$$

$$K_{HF_i} = \frac{x_{HF_i}\cdot x_{ME}}{x_{HF_{i-1}}\cdot x_{HF}}\cdot\frac{\gamma_{HF_i}\cdot\gamma_{ME}}{\gamma_{HF_{i-1}}\cdot\gamma_{HF}}. \qquad i>1 \qquad (10)$$

For calculating the species distribution in formaldehyde–water–methanol liquid mixtures at preset temperature and "overall" composition, the model requires five chemical equilibrium constants and UNIFAC parameters for all species present in the liquid phase. The algorithm used to calculate that oligomer distribution has been described previously (Albert, 1998).

Extended Raoult's law is applied for calculating the partial pressure and the total pressure (and the composition) of the vapor that coexists with that liquid:

$$p_i^s\cdot x_i\cdot\gamma_i = p\cdot y_i = p_i \qquad i = \mathrm{FA, W, ME, MG, HF} \qquad (11)$$

$$p = p_{FA} + p_W + p_{ME} + p_{MG} + p_{HF}. \qquad (12)$$

Therefore, besides the properties mentioned before (that is, chemical equilibrium constants and UNIFAC parameters), the model also requires vapor pressures of the pure components formaldehyde, water, methanol, methylene glycol, and hemiformal.

Determination of model parameters

Some model parameters were adopted from an earlier publication on the phase behavior of the binary formaldehyde–water system (Albert et al., 1999):

- The chemical-reaction equilibrium constant for reaction I in the vapor phase: $K_{MG,\mathrm{gas}}$ (cf. Table 4) and in the liquid phase (cf. Eq. 5).
- The chemical-reaction equilibrium constants for reaction II in the liquid phase K_{MG_2} and K_{MG_i} $(i \geq 3)$; cf. Table 4.
- The vapor pressures of water, formaldehyde, and methylene glycol (cf. Table 5).

Table 4. Chemical Equilibrium Constants $\ln K = A + B/(T/K)$

Reaction	A	B
$K_{MG_1,\mathrm{gas}}$	-16.984	5,233.2
K_{MG_2}	4.980×10^{-3}	869.5
K_{MG_n}, $n \geq 3$	1.908×10^{-2}	544.5
$K_{HF_1,\mathrm{gas}}$	-14.755	5,969.4
K_{HF_n}, $n \geq 2$	-4.966×10^{-1}	-491.3

Table 5. Antoine Coefficients for Pure Component Vapor Pressures $\ln(p^s/\mathrm{kPa}) = A + B/[(T/K) + C]$

Component	A	B	C
Formaldehyde	14.4625	$-2{,}204.13$	-30.0
Water	16.2886	$-3{,}816.44$	-46.13
Methanol	16.5725	$-3{,}626.55$	-34.29
Methylene glycol	19.5527	$-6{,}189.19$	-9.15
Hemiformal	19.5736	$-5{,}646.71$	0.0

Table 6. Division of Components in UNIFAC Groups

Component	UNIFAC Group	
Formaldehyde	1 CH_2O	
Water	1 H_2O	
Methanol	1 CH_3OH	
Methylene glycol	1 HO $(CH_2O)H$	
Hemiformal	1 CH_3O, 1 CH_2OH	
Poly(oxymethylene) glycols	$(n-1)$ CH_2O, 2 HO, 1 CH_2	$n \geq 2$
Poly(oxymethylene) hemiformals	$(n-1)$ CH_2O, 1 CH_3O, 1 CH_2OH	$n \geq 2$

Table 7. UNIFAC Size and Surface Parameters

Group	No.	R	Q
CH_2O	1	0.9183	0.780
H_2O	2	0.9200	1.400
$HO(CH_2O)H$	3	2.6744	2.940
OH	4	1.0000	1.200
CH_2	5	0.6744	0.540
CH_3O	6	1.1450	1.088
CH_3OH	7	1.4311	1.432
CH_2OH	8	1.2044	1.124

- Division of poly(oxymethylene) glycols into UNIFAC groups and UNIFAC parameters (size and surface parameters, cf. Tables 6 and 7; interaction parameters $(a_{i,j})$, (i, j) = CH_2O, H_2O, $HO(CH_2O)H$, OH, CH_2; cf. Table 8).

Extension to the ternary formaldehyde−water−methanol system requires additionally:

- The chemical-reaction equilibrium constant for reaction III in the vapor phase: $K_{HF,\mathrm{gas}}$. That equilibrium constant is adopted from Hasse (1990). It is based on experimental data for the vapor-phase density by Hall and Piret (1949) and Kogan (1979b); cf. Table 4.
- The chemical-reaction equilibrium constant for reaction IV, K_{HF_i} $(i \geq 2)$ for the formation of poly(oxymethylene) hemiformals in the liquid phase and the vapor pressure of hemiformal, p^s_{HF} were obtained from published experimental vapor−liquid and chemical-equilibrium data for the binary formaldehyde−methanol system (cf. Tables 4 and 5). The same procedure as that described before for fitting parameters in the formaldehyde−water system was used (Albert et al., 1999).
- Methanol was considered to be a single group, while hemiformal and poly(oxymethylene) hemiformals were divided into several groups (cf. Table 6). Size and surface parameters were taken from Hahnenstein et al. (1994b, cf. Table 7).
- Some UNIFAC interaction parameters were set to zero: $a_{CH_2O,CH_3O} = a_{CH_3O,CH_2O} = 0$
$a_{CH_2OH,CH_3OH} = a_{CH_3OH,CH_2OH} = 0$.

Furthermore some differences in interaction parameters were neglected:
$a_{CH_2O,CH_2OH} = a_{CH_3O,CH_3OH} = a_{CH_3O,CH_2OH} = a_{CH_2O,CH_3OH}$
$a_{CH_2OH,CH_2O} = a_{CH_3OH,CH_3O} = a_{CH_2OH,CH_3O} = a_{CH_3OH,CH_2O}$.

Therefore only two interaction parameters were fitted to experimental vapor-liquid equilibrium data for the binary formaldehyde−methanol system (cf. Table 8).

- UNIFAC parameters describing interactions between water and methanol were adopted from Maurer (1986).
- The remaining UNIFAC parameters describe interactions between groups in poly(oxymethylene) hemiformals and methanol on one side, with groups in poly(oxymethylene) gly-

Table 8. UNIFAC Interaction Parameters $a_{i,j}/K$

i	$j = 1$	2	3	4	5	6	7	8
1	−	774.81	189.21	237.7	83.36	0.0	238.4	238.4
2	-142.35	−	189.52	-229.1	300.0	-219.29	289.6	$a_{2,8}$
3	59.20	-191.82	−	-229.1	300.0	-142.35	289.6	289.6
4	28.06	353.5	353.5	−	156.4	112.82	-137.1	-137.1
5	251.5	1318.0	1318.0	986.5	−	447.77	697.2	697.2
6	0.0	423.75	774.81	1164.81	272.96	−	238.4	238.4
7	-128.6	-181.0	-181.0	249.1	16.51	-128.6	−	0.0
8	-128.6	$a_{8,2}$	-181.0	249.1	16.51	-128.6	0.0	−

$a_{i,j}/K = A + B/(T/K)$

Function	A	B
$a_{2,8}$	4.516×10^{2}	-1.141×10^{5}
$a_{8,2}$	-1.018×10^{3}	3.299×10^{5}

cols and water on the other side. Such interactions do not occur in the the binary systems.

- Some of the remaining interaction parameters were estimated: $a_{j,CH_2OH} = a_{j,CH_3OH}$; $a_{CH_2OH,j} = a_{CH_3OH,j}$. For $j =$ HO(CH_2O)H, OH, CH_2. These parameters were adopted from Maurer (1986): $a_{CH_3O,HO(CH_2O)H} = a_{CH_3O,H_2O}$; $a_{HO(CH_2O)H,CH_3O} = a_{H_2O,CH_3O}$.
- The residual interaction parameters were fitted to experimental data for vapor–liquid equilibrium of the ternary formaldehyde–water–methanol system. The results are given in Table 8.

Comparison with Experimental Results

Formaldehyde – methanol

Results of the new correlation were compared with the experimental data used to fit model parameters: vapor–liquid equilibrium data reported by Blazhin et al. (1976), Maurer (1986), Kogan and Ogorodnikov (1980a), and Hasse and Maurer (1991), and species distribution in liquid mixtures of formaldehyde and methanol from NMR-spectroscopic investigations by Hahnenstein et al. (1994a). Some typical comparisons are shown in Figures 3 and 4 for vapor–liquid equilibrium and in Figure 5 for species distribution.

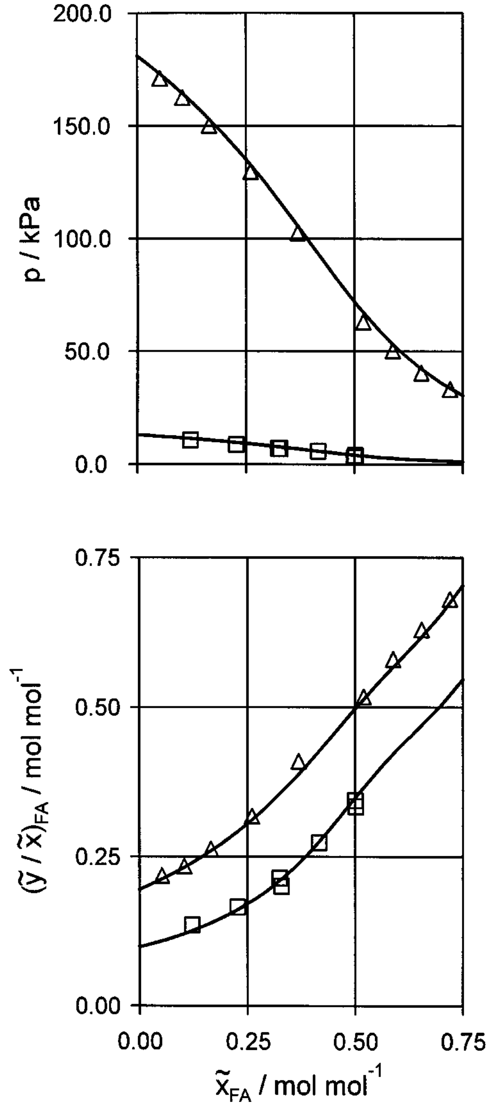

Figure 3. Formaldehyde–methanol.

Vapor–liquid equilibrium at 293 and 353 K; □, exp. (293 K), Hasse and Maurer (1991); △ , exp. (353 K), Kogan and Ogorodnikov (1980a); — , calc.

For comparison with experimental vapor–liquid equilibrium data by Kogan and Ogorodnikov (1980a) and by Hasse and Maurer (1991), calculations were performed with preset temperatures (from about 293 to about 353 K) and preset "overall" mol fractions of formaldehyde in the liquid phase (to about 0.7 mol · mol^{-1}). The partition coefficient of formaldehyde (that is, the ratio of "overall" mol fraction of formaldehyde in the vapor to that in the liquid phase) and the total pressure were calculated. Blazhin et al. (1976) performed experimental investigations at constant pressures (27 and 101 kPa). For comparison with those isobaric data, the "overall" mol fraction of formaldehyde in the liquid phase (to about 0.6 mol · mol^{-1}) and the pressure were preset and the partition coefficient of formaldehyde and the temperature

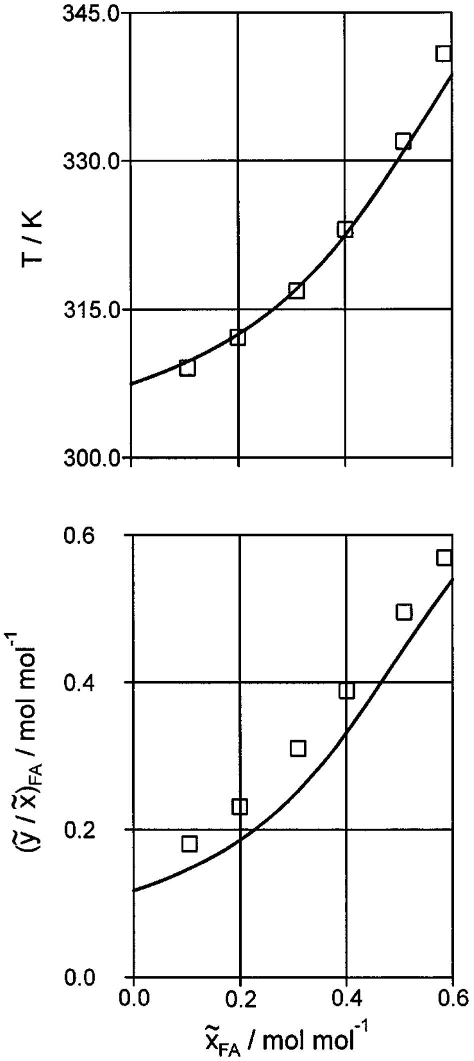

Figure 4. Formaldehyde–methanol.

Vapor–liquid equilibrium at 27 kPa; □, exp., Blazhin et al. (1976); —, calc.

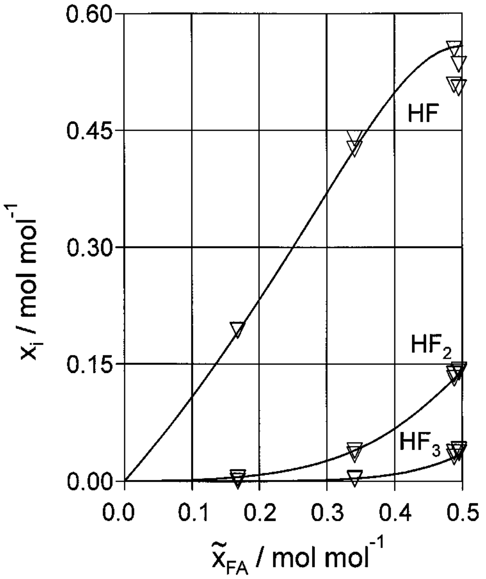

Figure 5. Formaldehyde–methanol.

Chemical reaction equilibrium at 276 K; ▽, exp., Hahnenstein et al. (1994a); —, calc.

were calculated. Deviations between correlation and experimental data are generally below 5% for the partition coefficient of formaldehyde, 3% for the total pressure, and 1 K for the boiling-point temperature. Maximum deviations are about 20% for the partition coefficient of formaldehyde (at 27 kPa and $\tilde{x}_{FA} \approx 0.1$ mol·mol^{-1}; cf. Figure 4), 13% for the total pressure (at 313 K and $\tilde{x}_{FA} \approx 0.12$ mol·mol^{-1}), and 3 K in the boiling-point temperature (at 101 kPa and $\tilde{x}_{FA} \approx 0.6$ mol·mol^{-1}). The calculations for true mol fraction of hemiformal and poly(oxymethylene) hemiformals agree with the results from NMR-spectroscopic investigations within the scatter of those experimental data.

Formaldehyde – water – methanol

The performance of the new model for representing vapor–liquid equilibrium of the ternary system were checked by comparing calculations with the new experimental data given in Tables 1 to 3 (cf. also Figures 1 and 2), as well as with published results by Blazhin et al. (1976), Kogan and Ogorodnikov (1980b), Maurer (1986), and Hasse and Maurer (1991).

Figure 6 shows a comparison with the experimental data by Blazhin et al. (1976) for $p = 27$ kPa in a triangular diagram while the comparison for $p = 101$ kPa is shown in Figure 8.

For these calculations the "overall" composition of the liquid phase and either the temperature or the pressure were preset, and the composition of the coexisting vapor phase and either the pressure or the temperature were calculated. In most cases the "slope" of a calculated tie-line connecting the points representing the compositions of the coexisting phases agrees with experiment within experimental uncertainty. Generally, predictions for the length of a tie-line deviate from the experimental data by not more than 2% (at maximum, by less than 10%). There are some larger deviations for only 101 kPa and for very small methanol concentrations in the liquid

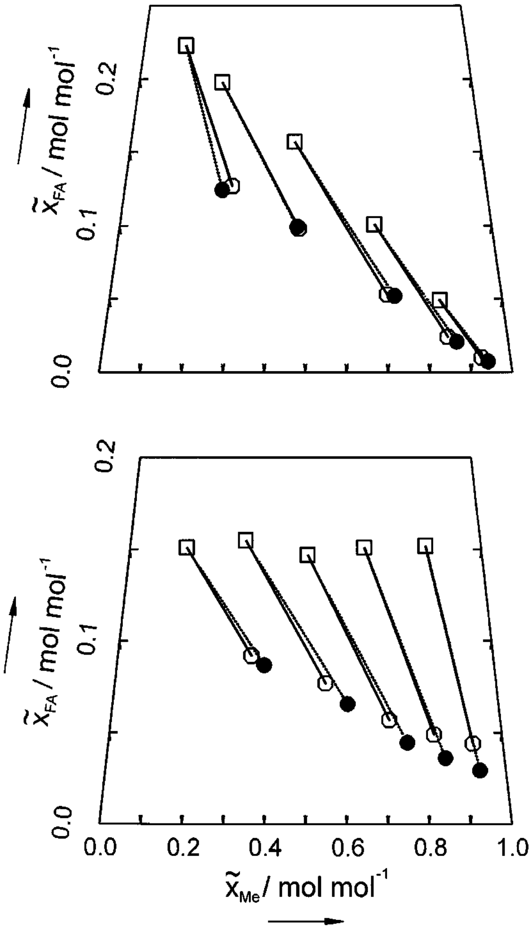

Figure 6. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 27 kPa (temperature between 313 and 337 K); □ and ○, exp. liquid and vapor phase, Blazhin et al. (1976); ● , calc. vapor phase.

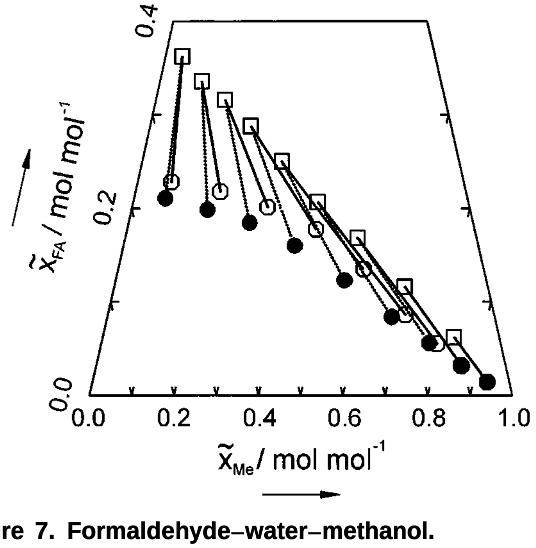

Figure 7. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 353 K (pressure between 47 and 158 kPa); □ and ○, exp. liquid and vapor phase, Kogan and Ogorodnikov (1980b); ● , calc. vapor phase.

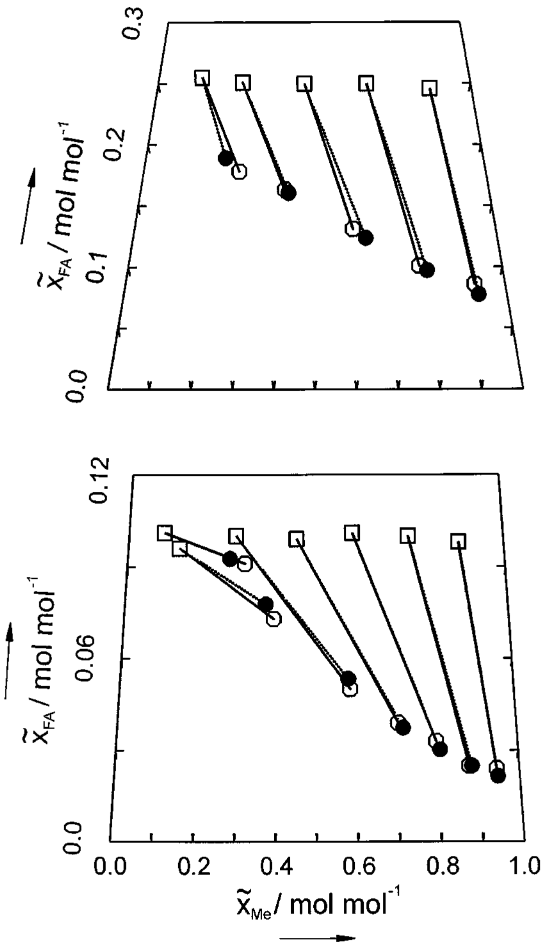

Figure 8. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 101 kPa (temperature between 343 and 369 K); □ and ○, exp. liquid and vapor phase, Blazhin et al. (1976); ● , calc. vapor phase.

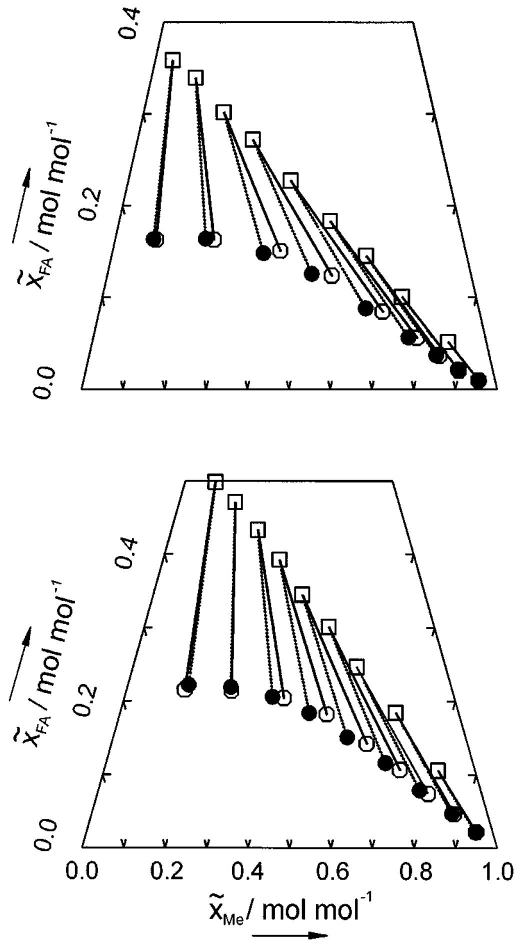

Figure 9. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 333 K (pressure between 17 and 76 kPa); □ and ○, exp. liquid and vapor phase, Kogan and Ogorodnikov (1980b); ●, calc. vapor phase.

phase. These deviations may be caused by the model or by experimental uncertainties.

Comparison with the experimental data by Kogan and Ogorodnikov (1980b) confirms the good agreement between the model and experimental data. Kogan and Ogorodnikov performed vapor–liquid equilibrium measurements at about 333, 343, and 353 K. For comparison with the model, the composition of the vapor phase and the total pressure in vapor–liquid equilibrium were calculated for preset temperature and liquid-phase ("overall") composition. A comparison between calculated and measured vapor-phase concentrations is shown in Figure 7 (for some typical results at 353 K), while more comparisons for 353 K as well as for 333 and 343 K are shown in Figures 9 to 11. The isotherm at 353 K was selected for the presentation in Figure 7 because the largest deviations from the experimental results for the composition of the vapor phase are observed at that temperature. While at low as well as at high water concentration in the liquid phase agreement between calculated and measured concentrations in the vapor phase is similar to that for the binary formaldehyde–water and formaldehyde–methanol systems, agreement declines increase at intermediate concentrations, that is, when $\tilde{x}_W \approx \tilde{x}_{ME}$. While predictions for the mol fraction of formaldehyde in the vapor phase are still good, the model underestimates the concentration of methanol in the vapor phase. The maximum relative deviation is about 10%. At lower temperatures (that is, at 293 and 313 K) the model can be compared with experimental results by Hasse and Maurer (1991). The agreement is excellent, as—with the exception of one single datum—the deviation is always smaller than the experimental uncertainty. That statement also holds for most deviations between predictions and experimental results for the composition of the vapor phase reported by Maurer (1986), although in a few cases the differences are larger than the estimated experimental uncertainty.

It was previously reported (Hasse and Maurer, 1991) that adding small amounts of methanol to a dilute aqueous formaldehyde solution might result in a large increase in the partition coefficient of formaldehyde in vapor–liquid equilibrium. The model of Maurer (1986) already predicted the existence of a maximum when the partition coefficient of formaldehyde is plotted at constant temperature against the "overall" concentration of methanol. However, lack of sufficient experimental data did not allow a check to be made of either the existence of such a maximum or to compare predictions with experiment. The new data presented in Tables

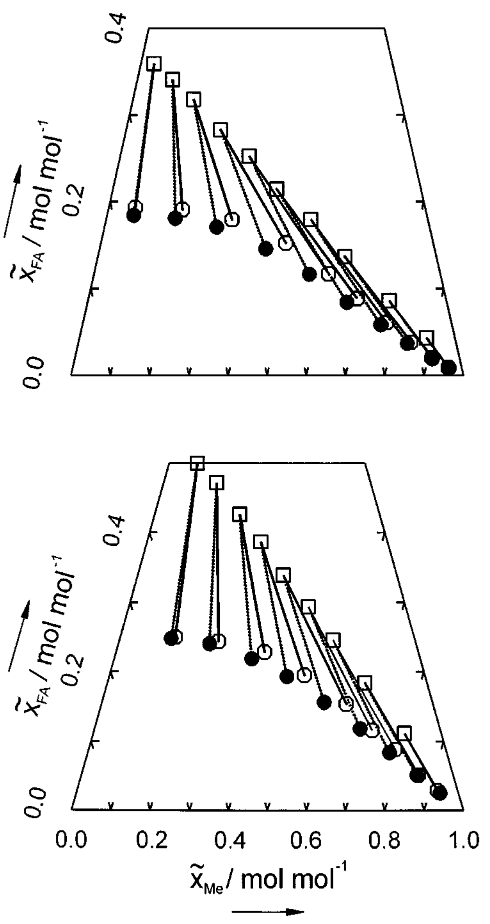

Figure 10. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 343 K (pressure between 28 and 114 kPa); □ and ○, exp. liquid and vapor phase, Kogan and Ogorodnikov (1980b); ●, calc. vapor phase.

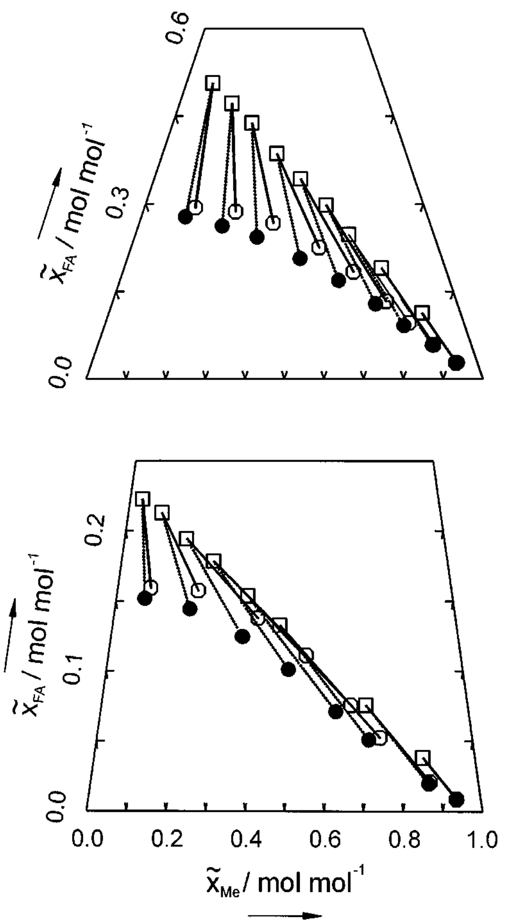

Figure 11. Formaldehyde–water–methanol.

Vapor–liquid equilibrium at 353 K (pressure between 45 and 161 kPa); □ and ○, exp. liquid and vapor phase, Kogan and Ogorodnikov (1980b); ●, calc. vapor phase.

1 to 3 confirm the presence of a maximum and also allow a comparison with calculations. That comparison is shown in Tables 1 to 3. The standard deviation for the mol fraction of formaldehyde in the vapor phase is between 5 and 8% at very small formaldehyde concentrations in the liquid ($\tilde{x}_{FA} < 0.01$ mol·mol^{-1}) and 3% at higher formaldehyde concentrations ($\tilde{x}_{FA} \approx 0.1$ mol·mol^{-1}). The standard deviation for the predicted mol fraction of methanol in the vapor phase is between about 0.6% and about 12%. The larger number is mainly due to some larger deviations at very small methanol concentrations ($\tilde{x}_{ME} < 0.04$ mol·mol^{-1}). The maximum standard deviation for the total pressure is about 2%. Thus most predictions agree with experiment within experimental uncertainty. The model also gives a reliable representation of the experimental results for the partition coefficient of formaldehyde at 313 K, reported by Hasse and Maurer (1991). The relative deviation (for preset overall composition of the liquid phase) is below 6%.

Predictions of Enthalpy Changes Upon Partial Evaporation of Ternary Mixtures Formaldehyde–Water–Methanol

Experimental results for the enthalpy change accompanying the partial vaporization of liquid mixtures of formaldehyde, water, and methanol were reported by Liu et al. (1992). The new model predicts those enthalpy differences as well as the previous model (cf. Liu et al., 1992), that is, predicted enthalpy changes agree with the experimental results within 10%

Conclusion

A thermodynamic framework for modeling the vapor–liquid equilibrium in aqueous and methanolic solutions of formaldehyde is revised using new experimental data, particularly on the influence of small amounts of methanol on the volatility of (small amounts) of formaldehyde in aqueous solutions. Also, a recently published revision of that model for the binary formaldehyde–water system is extended to describe the formaldehyde–methanol and formaldehyde–water–methanol systems. The model quantitatively describes the vapor–liquid equilibrium of methanolic solutions, including the strong influence of small amounts of methanol on the volatility of formaldehyde in aqueous solutions.

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Notation

A = parameter
B = parameter
C = parameter
K = chemical equilibrium constant
p = pressure
p^{θ} = standard pressure (101.325 kPa)
Q = UNIFAC surface parameter
R = UNIFAC size parameter
T = temperature
W = water
x = true mol fraction in liquid phase
$\tilde{x}$ = overall mol fraction in liquid phase
$\tilde{x}^*_{ME} = \tilde{x}_{ME}/(\tilde{x}_{ME} + \tilde{x}_W)$
y = true mol fraction in vapor phase
$\tilde{y}$ = overall mol fraction in vapor phase
$\tilde{y}_{FA}/\tilde{x}_{FA}$ = partition coefficient of formaldehyde
Δ = difference
γ = activity coefficient normalized according to Raoult's law
$\tilde{\xi}$ = overall mass fraction in liquid phase

Subscripts and superscripts

i = component i
W = water
s = saturation

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