Revised Vapor-Liquid Equilibrium Model for Multicomponent Formaldehyde Mixtures

Formaldehyde is one of the most important intermediate products of the chemical industry. Due to its high reactivity, it is commonly handled in aqueous or methanolic solutions. In these solutions, formaldehyde is dissolved chemically. Therefore, modeling thermodynamic properties of aqueous and methanolic formaldehyde-containing mixtures require the consideration of chemical reactions and physical effects. A recently published physico-chemical model (Maurer, 1986) for the description of vapor-liquid equilibria of these systems is tested and improved on the basis of about 140 new experimental data points for mixtures containing formaldehyde, water, methanol, and trioxane at temperatures between 320 and 380 K and pressures below 100 kPa. Improvements are achieved by fitting some of those binary interaction parameters, which formerly had to be estimated due to the lack of experimental data. The revised model is able to reliably predict vapor-liquid equilibria in multicomponent formaldehyde-containing mixtures.

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Introduction

Due to its high reactivity, formaldehyde is used in technical processes mainly in aqueous solutions that often also contain methanol. The concentration of monomeric formaldehyde in these solutions is very low, as formaldehyde is dissolved mainly chemically forming polymers with water and methanol. The most important chemical reactions in aqueous and methanolic formaldehyde solutions are given in Table 1. These reactions have an essential influence on the vapor–liquid equilibrium, which has to be taken into consideration in the design of separation equipment. Further reactions are important in certain pH ranges, especially at temperatures above 400 K (Walker, 1964; Ullmann, 1988).

Equilibrium models for formaldehyde-containing systems have been proposed by several researchers (Brandani, 1976, 1980, 1985, 1987; Tunik et al., 1977; Kogan, 1979, 1980; Maurer, 1986), but only the model of Maurer takes into account intermolecular forces as well as the chemical reactions. As a group contribution method for the excess Gibbs energy is used, the model of Maurer can be extended in a straightforward manner to the description of multicomponent formaldehyde-containing mixtures. This is of considerable industrial interest, as it allows predictions of vapor–liquid equilibria in mixtures containing various downstream products of formaldehyde. For example, mixtures with trioxane, the basic chemical for the polyacetal resin production, can be treated. Maurer (1986) has shown that his model is able to reliably predict vapor–liquid equilibria in the ternary systems, formaldehyde/water/methanol and formaldehyde/water/trioxane, from binary data alone. These investigations have been extended in this work to the quaternary system, formaldehyde/water/methanol/trioxane. Although this quaternary system is of considerable importance in producing polyacetal resins, no experimental data on its vapor–liquid equilibria have been published. Therefore, the model performance for this system could not be tested.

This paper reports on the new experimental data for vapor–liquid equilibria in binary and multicomponent mixtures of formaldehyde, water, methanol, and trioxane at temperatures between 323 and 377 K and pressures below 100 kPa. The measurements are used to revise and extend the parameter set of the model of Maurer (1986) and to test predictions for quaternary vapor–liquid equilibria.

Measurements

Measurements of vapor–liquid equilibria in formaldehyde-containing systems require special techniques to ensure that equilibrium is reached despite slow chemical reactions occurring

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Table 1. Most Important Reactions in Aqueous and Methanolic Formaldehyde Solutions

Formation of methylene glycol (MG):

$$CH_2O + H_2O \rightleftharpoons HO(CH_2O)H$$

Formation of polyoxymethylene glycols (MG_n):

$$HO(CH_2O)_{n-1}H + HO(CH_2O)H \rightleftharpoons HO(CH_2O)_nH + H_2O \quad (n \geq 2)$$

Formation of hemiformal (HF):

$$CH_2O + CH_3OH \rightleftharpoons H_3CO(CH_2O)H$$

Formation of polyoxymethylene hemiformals (HF_n):

$$HO(CH_2O)_{n-1}CH_3 + HO(CH_2O)CH_3 \rightleftharpoons HO(CH_2O)_nCH_3 + CH_3OH \quad (n \geq 2)$$

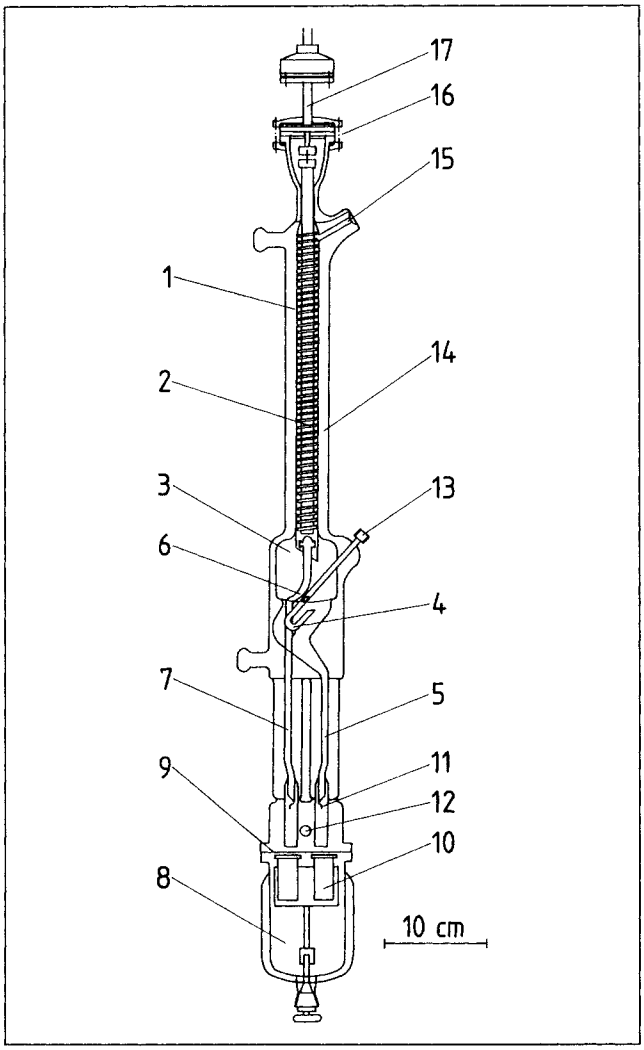

Figure 1. Vapor–liquid equilibrium apparatus.

1. double mantled tube
2. coil
3. phase separation chamber
4. siphon
5. cooler
6. gas-phase outlet
7. condenser
8. sample collection vessel
9. plane grinding
10. sample bottles
11. nose
12. connection to pressure control
13. thermometer connection
14. thermostated liquid
15. feed
16. magnetic clutch
17. motor shaft

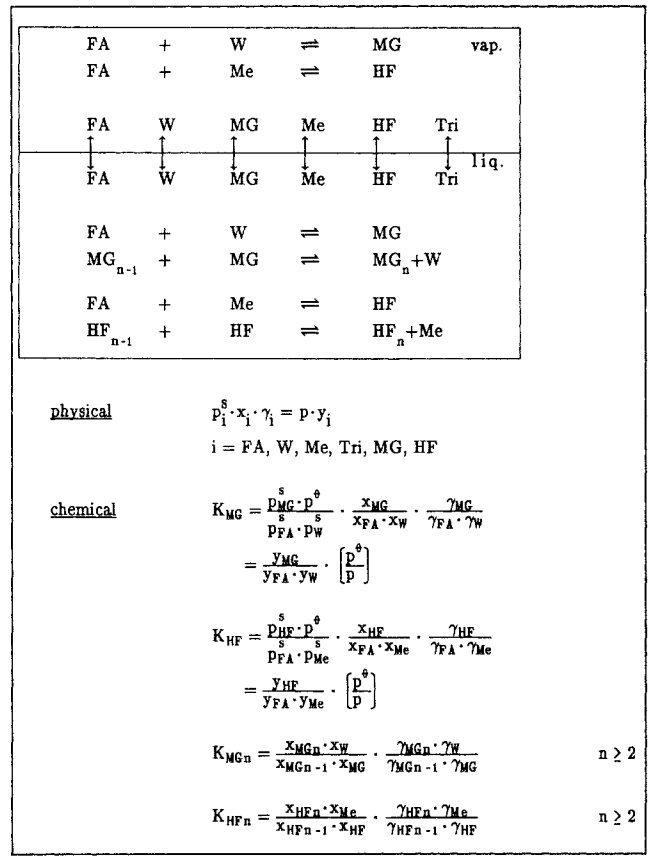

Figure 2. Vapor–liquid equilibrium in the formaldehyde/water/methanol/trioxane system.

in the liquid phase. For the measurements reported here, a thin film evaporator (Figure 1) was used. A rotating coil spreads the liquid feed as a thin film on the inner surface of a vertical tube, which is thermostated by a liquid. By properly adjusting temperature, pressure, feed flow rate, and speed of rotation, it is possible to achieve the high residence times (≥2 min) and low evaporation ratios (≤10% of the feed) necessary to reach equilibrium in the wet vapor leaving the tube. It was proved that equilibrium is reached in the apparatus at temperatures down to about 320 K. At lower temperatures, equilibrium cannot always be ensured, as the reaction rates become very small.

The gas and the liquid phase are separated, cooled, and

Table 2. Division of the Components of the Formaldehyde/Water/Methanol/Trioxane System into UNIFAC Groups

Component	Groups	
FA	CH_2O	
W	H_2O	
Me	CH_3OH	
Tri	$C_3H_6O_3$	
MG	$HOCH_2OH$	
HF	1 CH_3O, 1 CH_2OH	
MG_n	2 HO, $(n-1)$ CH_2O, 1 CH_2	$n \geq 2$
HF_n	1 CH_3O, $(n-1)$ CH_2O, 1 CH_2OH	$n \geq 2$

Table 3a. Vapor-Liquid Equilibrium in the Methanol/Trioxane System at 93.3 kPa (Experimental Results, Recirculating Still)

T K	x_{Tri} mol/mol	x_{Me} mol/mol	y_{Tri} mol/mol	y_{Me} mol/mol
335.71	0.0054	0.9946	0.0040	0.9960
335.89	0.0280	0.9720	0.0185	0.9815
336.13	0.0577	0.9423	0.0339	0.9661
336.41	0.0934	0.9066	0.0492	0.9508
336.67	0.1186	0.8814	0.0573	0.9427
336.99	0.1498	0.8502	0.0664	0.9336
337.36	0.1753	0.8247	0.0728	0.9272
337.32	0.1853	0.8147	0.0748	0.9252
337.96	0.2354	0.7646	0.0873	0.9127
338.67	0.3015	0.6985	0.1020	0.8980
339.60	0.3824	0.6176	0.1097	0.8903
340.00	0.4117	0.5883	0.1157	0.8843
341.07	0.4828	0.5172	0.1273	0.8727
341.88	0.5292	0.4708	0.1440	0.8560
342.22	0.5406	0.4594	0.1461	0.8539
344.49	0.6289	0.3711	0.1710	0.8290
345.59	0.6589	0.3411	0.1859	0.8141
347.91	0.7234	0.2766	0.2158	0.7842
353.46	0.8092	0.1908	0.2878	0.7122
354.63	0.8269	0.1731	0.3074	0.6926
365.73	0.9203	0.0797	0.4971	0.5029
365.92	0.9238	0.0762	0.5020	0.4980
367.89	0.9361	0.0639	0.5391	0.4609
371.42	0.9539	0.0461	0.6179	0.3821
377.23	0.9762	0.0238	0.7664	0.2336

collected in small bottles on a turnable bottle holder. The pressure is applied by an inert gas through the sample collection vessel and measured with a mercury manometer with an accuracy of about 0.1 kPa. The temperature is measured with a platinum resistance thermometer in the phase separation chamber with an accuracy of about 0.1 K.

Table 3b. Vapor-Liquid Equilibrium in the Methanol/Trioxane System at 333 K (Experimental Results, Thin Film Evaporator)

T K	p kPa	x_{Tri} mol/mol	x_{Me} mol/mol	y_{Tri} mol/mol	y_{Me} mol/mol
333.23	82.89	0.0101	0.9899	0.0076	0.9924
333.11	82.71	0.0105	0.9895	0.0079	0.9921
333.09	82.66	0.0199	0.9801	0.0141	0.9859
333.14	82.27	0.0283	0.9717	0.0192	0.9808
333.20	81.04	0.0327	0.9673	0.0222	0.9778

For analyzing formaldehyde, the sodium sulfite method was used (relative errors less than 2%). Methanol and trioxane were analyzed by gas chromatography (relative errors less than 4%). As the masses of the liquid- and gas-phase samples were determined and the concentrations in both phases and the feed were analyzed, mass balances provided a means to check the analysis. No discrepancies exceeding the given analytical uncertainties were found.

For most of the measurements in the methanol/trioxane and the water/trioxane system instead of the thin film evaporator, a recirculating still, described by Hasse (1990), was used. The previously given values for the experimental uncertainties also hold for these measurements.

All chemicals were purchased from Merck or Riedel de Haen in the best available quality and used without further purification as gas chromatographic analysis showed only trace amounts of impurities. Formaldehyde solutions were prepared by dissolving paraformaldehyde in water or methanol at elevated temper-

Table 4. Vapor-Liquid Equilibrium in the Water/ Methanol/Trioxane System at 323, 343 and 363 K (Experimental Results)

T K	p kPa	x_W mol/mol	x_{Me} mol/mol	x_{Tri} mol/mol	y_W mol/mol	y_{Me} mol/mol	y_{Tri} mol/mol
323.17	27.41	0.7633	0.2175	0.0192	0.3743	0.5748	0.0509
323.15	32.00	0.6531	0.3232	0.0237	0.2755	0.6788	0.0457
323.12	36.97	0.5174	0.4536	0.0290	0.2466	0.7128	0.0406
323.11	44.35	0.2795	0.6880	0.0325	0.1122	0.8573	0.0305
323.16	41.53	0.3794	0.5880	0.0326	0.1789	0.7871	0.0340
343.16	49.52	0.9082	0.0800	0.0118	0.5949	0.3544	0.0507
343.16	44.97	0.9299	0.9524	0.0177	0.6559	0.2601	0.0840
343.31	64.23	0.7928	0.1838	0.0234	0.3872	0.5519	0.0609
343.20	70.16	0.7206	0.2545	0.0249	0.3220	0.6268	0.0512
343.27	78.21	0.6176	0.3546	0.0278	0.2530	0.7038	0.0432
343.23	85.30	0.5001	0.4690	0.0309	0.2042	0.7587	0.0371
343.19	46.26	0.9101	0.0511	0.0388	0.6090	0.2418	0.1492
343.27	46.86	0.9046	0.0537	0.0417	0.5821	0.2513	0.1666
343.27	59.33	0.8089	0.1432	0.0479	0.4230	0.4614	0.1156
343.19	72.47	0.6951	0.2551	0.0498	0.3236	0.5959	0.0805
343.19	64.88	0.7379	0.2061	0.0560	0.3394	0.5505	0.1101
343.24	83.76	0.5038	0.4265	0.0697	0.2131	0.7159	0.0710
343.17	91.42	0.3987	0.5277	0.0736	0.1714	0.7642	0.0644
363.14	88.34	0.9652	0.0295	0.0053	0.7957	0.1728	0.0315
363.19	82.70	0.9724	0.0206	0.0070	0.8234	0.1322	0.0444
363.13	95.36	0.9429	0.0478	0.0093	0.7071	0.2490	0.0439
363.57	87.81	0.9610	0.0251	0.0139	0.7869	0.1412	0.0719
363.61	90.17	0.9564	0.0223	0.0213	0.7715	0.1268	0.1017

atures and separating solid residues by filtration. For more experimental details, see Hasse's work (1990).

Model

The model used in this work to correlate and predict vapor–liquid equilibria in formaldehyde-containing systems has been described in detail by Maurer (1986). Therefore, only a brief survey is given here. Figure 2 shows some of the basic assumptions of the model for the formaldehyde/water/methanol/trioxane system and the set of physical and chemical conditions for the vapor–liquid equilibrium.

The formation of methylene glycol *MG*, hemiformal *HF*, polyoxymethylene glycols MG_n, and polyoxymethylene hemiformals HF_n are taken into account. Due to the low vapor pressures of the polyoxymethylene glycols and hemiformals, their concentrations in the gas phase can be neglected. As the total pressure in formaldehyde processing units rarely exceeds 0.5 MPa, the gas phase is treated as a mixture of ideal gases. Nonidealities in the liquid phase are taken into consideration by using the UNIFAC group contribution method (Fredenslund et al., 1982). Table 2 indicates how the components of the quaternary system, formaldehyde/water/methanol/trioxane, are divided into groups.

Applying the model requires the following information:

- Vapor pressures of pure formaldehyde, water, methanol, methylene glycol, hemiformal and trioxane
- Chemical equilibrium constants for the reactions given in Table 1
- UNIFAC size, surface and interaction parameters.

In a previous publication (Maurer, 1986), the procedure to determine these parameters has been described and numerical values for all parameters, except those for interactions between trioxane as one group and methanol, CH_3O, or CH_2OH as the second one, were given. The missing interaction parameters were determined in this work: parameters for the interaction between trioxane and methanol were evaluated using two sets of vapor–liquid equilibrium data for the methanol/trioxane system

Table 5a. Vapor-Liquid Equilibrium in the Water/Trioxane System at 93.3 kPa (Experimental Results, Recirculating Still)

T K	x_{Tri} mol/mol	xxQ_W mol/mol	y_{Tri} mol/mol	y_W mol/mol
370.30	0.0024	0.9976	0.0171	0.9829
368.81	0.0125	0.9875	0.0771	0.9229
364.60	0.0679	0.9321	0.2404	0.7596
364.29	0.0877	0.9123	0.2533	0.7467
362.84	0.1777	0.8223	0.3088	0.6912
362.70	0.2061	0.7939	0.3124	0.6876
362.67	0.2366	0.7634	0.3265	0.6735
362.61	0.2562	0.7438	0.3262	0.6738
362.63	0.2918	0.7082	0.3320	0.6680
362.60	0.3261	0.6739	0.3317	0.6683
362.60	0.3636	0.6364	0.3561	0.6439
362.86	0.5109	0.4891	0.3619	0.6381
363.10	0.5487	0.4513	0.3809	0.6191
363.30	0.5847	0.4153	0.3887	0.6113
363.85	0.6446	0.3554	0.3899	0.6101
365.57	0.7333	0.2667	0.4320	0.5680
368.00	0.7976	0.2024	0.4910	0.5090
370.55	0.8507	0.1493	0.5589	0.4411
374.00	0.9001	0.0999	0.6370	0.3630
377.45	0.9482	0.0518	0.7509	0.2491

Table 5b. Vapor-Liquid Equilibrium in the Water/Trioxane System at 343 K (Experimental Results, Thin Film Evaporator)

T K	p kPa	x_{Tri} mol/mol	x_W mol/mol	y_{Tri} mol/mol	y_W mol/mol
342.94	30.89	0.00094	0.99906	0.0080	0.9920
343.19	30.80	0.00143	0.99857	0.0128	0.9872
342.93	31.35	0.00281	0.99719	0.0238	0.9762
343.22	31.47	0.00375	0.99625	0.0305	0.9695
342.87	32.01	0.00608	0.99392	0.0506	0.9494
343.09	32.38	0.00805	0.99195	0.0640	0.9360

(cf. Tables 3a and 3b). UNIFAC parameters for interactions between trioxane and CH_3O and CH_2OH were initially estimated by using the following relationships:

$$a_{Tri,CH_3O} = a_{Tri,CH_2O} \quad a_{Tri,CH_2OH} = a_{Tri,Me}$$
$$a_{CH_3O,Tri} = a_{CH_2O,Tri} \quad a_{CH_2OH,Tri} = a_{Me,Tri}$$

Predictions based on these parameters deviated systematically from experimental results for the quaternary system, formaldehyde/water/methanol/trioxane. For fixed temperature and liquid-phase composition, calculated vapor-phase concentrations of trioxane were too small, about 20–30% (at absolute concentrations of about 0.05 mol/mol), whereas all other concentrations and the pressure were predicted reliably. Therefore, it was assumed that parameters describing properties of trioxane or its interactions with other groups had to be revised. To check this assumption, a number of vapor–liquid equilibria were measured for the nonreacting system water/methanol/trioxane. The comparison with predictions for this system revealed discrepancies very similar to those observed for the quaternary system and thus confirmed the assumption.

Experimental Results for Improving and Extending the Model

Tables 3 and 4 give new experimental results for the vapor–liquid equilibrium in the binary system, methanol/trioxane, and the ternary system, water/methanol/trioxane. For these systems, the UNIFAC method merges into the UNIQUAC method, due to the selection of groups (Table 2). UNIFAC interaction parameters were either taken from literature or, in the case of

Table 6. UNIFAC Parameters for Interactions between Trioxane and Other Groups

$q_{Tri} = 3.3, \quad r_{Tri} = 2.754$			
Group i	$a_{Tri,i}$ K	$a_{i,Tri}$ K	Comments
H_2O	389.13	83.00	This work (Revised or New)
CH_3OH	278.68	−28.73	
$HOCH_2OH$	187.74	11.76	
CH_2OH	392.16	−187.67	
CH_2O	0	0	Maurer (1986)
CH_3OH	0	0	
OH	237.70	28.06	
CH_2	83.36	251.50	

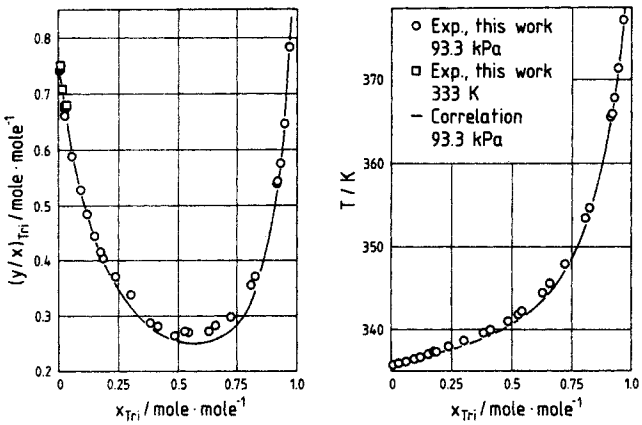

Figure 3. Vapor–liquid equilibrium in the methanol/trioxane system.

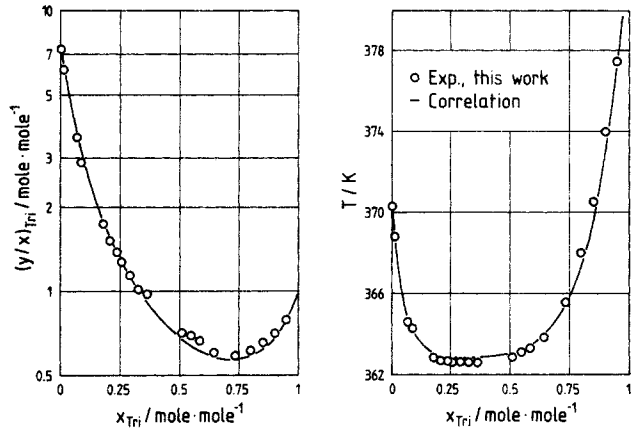

Figure 4. Vapor–liquid equilibrium in the water/trioxane system at 93.3 kPa.

methanol/trioxane, determined from the binary vapor–liquid equilibrium data in the Tables 3a and 3b with a maximum likelihood method (Prausnitz et al., 1980). When those parameters are used to predict the new vapor–liquid equilibrium data in the ternary system, water/methanol/trioxane (Table 4), a systematic influence of the temperature on the deviations between correlated and measured vapor–liquid equilibria is observed, even though the temperature range does not exceed 40 K. A correction is possible either by introducing temperature-dependent interaction parameters or by correcting the number of the surface parameter of trioxane, as the UNIQUAC model predicts an effect of the surface parameter q on the influence of temperature on the activity coefficient. For example, for the activity coefficient of a compound 1, infinitely diluted in the solvent 2, one finds:

$$\left(\frac{\partial \ln \gamma_{1,2}^{\infty}}{\partial T}\right) \sim q_1.$$

Originally the surface parameter of the CH_2O group was taken from Fredenslund et al. (1982) to be $q_{CH_2O} = 0.78$. By changing that number to $q_{CH_2O} = 1.1$, as it follows from the same work of Fredenslund for the CH_2O group in tetrahydrofuran, the surface parameter of trioxane rises from 2.34 to 3.3. This leads to a more favorable, stronger influence of

Table 7. Vapor-Liquid Equilibrium in the Formaldehyde/Methanol/Trioxane System: Experimental Results vs. Calculations

				$\tilde{y}_{FA}$			$\tilde{y}_{Me}$			$\tilde{y}_{Tri}$			p		
T	$\tilde{x}_{FA}$	$\tilde{x}_{Me}$	$\tilde{x}_{Tri}$	Exp.	Calc.	100 D	Exp.	Calc.	100 D	Exp.	Calc.	100 D	Exp.	Calc.	100 D
K	mol/mol			mol/mol			mol/mol			mol/mol			kPa		
333.2	0.148	0.765	0.087	0.033	0.030	−6.5	0.915	0.918	0.2	0.052	0.052	0.4	68.25	69.75	2.2
333.3	0.263	0.672	0.065	0.070	0.072	3.7	0.880	0.879	−0.2	0.050	0.049	−0.9	56.94	57.81	1.5
333.1	0.395	0.542	0.063	0.146	0.152	4.0	0.789	0.782	−0.8	0.065	0.066	1.0	39.27	40.42	2.9
333.1	0.159	0.721	0.120	0.033	0.034	2.2	0.899	0.899	0.0	0.068	0.067	−1.6	65.77	67.01	1.9
$100\,\overline{D}$				0.8			−0.2			−0.3			2.1		
$100\,S_D$				5.0			0.5			1.2			0.6		

Table 8. Vapor-Liquid Equilibrium in the Formaldehyde/Water/Trioxane System: Experimental Results vs. Predictions

				$\tilde{y}_{FA}$			$\tilde{y}_{W}$			$\tilde{y}_{Tri}$			p		
T	$\tilde{x}_{FA}$	$\tilde{x}_{W}$	$\tilde{x}_{Tri}$	Exp.	Calc.	100 D	Exp.	Calc.	100 D	Exp.	Calc.	100 D	Exp.	Calc.	100 D
K	mol/mol			mol/mol			mol/mol			mol/mol			kPa		
343.2	0.037	0.957	0.006	0.035	0.032	−10.1	0.916	0.918	0.2	0.049	0.050	2.8	32.49	32.72	0.7
343.2	0.060	0.935	0.005	0.051	0.049	−4.6	0.917	0.916	−0.1	0.032	0.035	11.4	32.06	32.21	0.5
343.2	0.108	0.887	0.005	0.080	0.076	−5.0	0.882	0.887	0.5	0.038	0.037	−1.1	31.96	31.96	0.0
343.2	0.139	0.857	0.004	0.098	0.092	−6.5	0.870	0.877	0.8	0.032	0.031	−2.4	31.56	31.50	−0.2
$100\,\overline{D}$				−6.5			0.4			2.7			0.2		
$100\,S_D$				2.5			0.4			6.2			0.4		

Table 9. Vapor-Liquid Equilibrium in the Formaldehyde/Water/Methanol/Trioxane System: Experimental Results vs. Predictions

					$\tilde{y}_{FA}$			$\tilde{y}_W$		
T	$\tilde{x}_{FA}$	$\tilde{x}_W$	$\tilde{x}_{Me}$	$\tilde{x}_{Tri}$	Exp.	Calc.	100 D	Exp.	Calc.	100 D
K	mol/mol				mol/mol			mol/mol		
343.0	0.037	0.925	0.025	0.013	0.032	0.031	−4.1	0.786	0.773	−1.8
343.1	0.041	0.924	0.021	0.014	0.036	0.034	−6.8	0.796	0.786	−1.2
343.1	0.042	0.930	0.016	0.012	0.038	0.035	−7.6	0.808	0.812	0.5
343.0	0.051	0.254	0.654	0.041	0.012	0.011	−6.0	0.124	0.117	−5.4
343.1	0.055	0.878	0.061	0.006	0.040	0.043	6.2	0.736	0.681	−7.3
343.2	0.058	0.560	0.356	0.026	0.019	0.020	5.3	0.312	0.285	−8.7
343.0	0.062	0.202	0.663	0.073	0.013	0.013	0.1	0.121	0.097	−20.0
343.2	0.064	0.253	0.578	0.105	0.015	0.015	−4.8	0.144	0.127	−11.8
343.1	0.069	0.460	0.458	0.013	0.021	0.021	−0.1	0.231	0.227	−1.9
342.9	0.073	0.902	0.021	0.004	0.062	0.057	−7.3	0.837	0.823	−1.6
343.0	0.075	0.907	0.012	0.006	0.062	0.058	−7.2	0.856	0.849	−0.8
343.0	0.078	0.838	0.065	0.019	0.059	0.053	−9.8	0.666	0.652	−2.0
343.1	0.079	0.246	0.578	0.097	0.019	0.019	−2.8	0.160	0.127	−20.8
343.1	0.091	0.447	0.445	0.017	0.027	0.028	6.0	0.208	0.233	12.1
343.1	0.095	0.301	0.567	0.037	0.024	0.024	1.1	0.153	0.154	0.2
343.1	0.104	0.778	0.102	0.016	0.070	0.064	−8.4	0.610	0.588	−3.6
343.1	0.111	0.231	0.642	0.016	0.028	0.027	−3.6	0.140	0.118	−15.4
343.1	0.112	0.843	0.030	0.015	0.082	0.074	−10.3	0.756	0.751	−0.6
343.0	0.116	0.784	0.077	0.023	0.078	0.070	−9.5	0.652	0.629	−3.4
343.2	0.118	0.833	0.038	0.011	0.085	0.079	−7.1	0.744	0.745	0.3
343.2	0.138	0.529	0.317	0.016	0.055	0.055	−0.3	0.402	0.328	−18.3
343.2	0.156	0.225	0.576	0.043	0.041	0.043	3.7	0.152	0.131	−13.8
343.1	0.158	0.697	0.129	0.016	0.100	0.087	−13.1	0.586	0.557	−4.7
343.1	0.161	0.762	0.056	0.021	0.104	0.092	−11.5	0.652	0.678	3.9
343.2	0.180	0.618	0.192	0.010	0.099	0.091	−8.2	0.495	0.475	−4.2
343.2	0.205	0.679	0.106	0.010	0.130	0.111	−14.3	0.631	0.614	−2.7
343.2	0.218	0.203	0.562	0.017	0.068	0.068	−0.9	0.150	0.133	−11.7
343.2	0.235	0.219	0.494	0.052	0.075	0.079	4.9	0.196	0.158	−19.4
343.2	0.242	0.125	0.527	0.106	0.077	0.078	1.4	0.067	0.095	42.4
343.2	0.246	0.082	0.653	0.019	0.071	0.073	2.7	0.063	0.056	−11.7
343.2	0.247	0.206	0.450	0.097	0.085	0.087	3.5	0.155	0.163	5.4
343.2	0.250	0.135	0.598	0.017	0.075	0.078	4.8	0.104	0.094	−9.9
343.2	0.250	0.127	0.563	0.060	0.078	0.079	2.0	0.074	0.093	24.8
343.2	0.300	0.094	0.587	0.019	0.097	0.102	6.1	0.103	0.074	−28.6
363.1	0.038	0.914	0.035	0.013	0.040	0.042	4.6	0.775	0.748	−3.6
363.2	0.051	0.913	0.029	0.007	0.058	0.056	−2.2	0.764	0.786	2.6
363.1	0.057	0.885	0.052	0.006	0.057	0.058	3.0	0.727	0.717	−1.4
363.2	0.059	0.894	0.030	0.017	0.058	0.060	4.1	0.772	0.750	−2.8
363.1	0.096	0.805	0.089	0.010	0.080	0.079	−1.1	0.640	0.631	−1.3
363.2	0.118	0.840	0.027	0.015	0.105	0.104	−1.1	0.750	0.753	0.3
363.2	0.127	0.835	0.029	0.009	0.115	0.112	−2.1	0.752	0.766	1.8
363.0	0.138	0.811	0.040	0.011	0.119	0.115	−3.2	0.726	0.733	0.9
363.1	0.173	0.714	0.102	0.011	0.128	0.122	−4.7	0.622	0.616	−1.0
363.1	0.175	0.683	0.127	0.015	0.123	0.117	−5.3	0.584	0.573	−2.0
363.2	0.222	0.733	0.035	0.010	0.169	0.160	−5.7	0.705	0.725	2.8
363.1	0.236	0.580	0.161	0.023	0.147	0.139	−5.3	0.537	0.517	−3.7
363.1	0.257	0.689	0.038	0.016	0.172	0.171	−0.7	0.695	0.693	−0.3
363.2	0.294	0.501	0.176	0.029	0.171	0.164	−3.8	0.529	0.485	−8.4
363.0	0.310	0.537	0.125	0.028	0.188	0.177	−5.9	0.565	0.547	−3.2
		$100\,\bar{D}$				−2.6			−3.3	
		$100\,S_D$				5.5			11.0	

temperature on the activity coefficient of trioxane. Therefore, $q_{Tri} = 3.3$ was adopted for all further calculations.

The change in the surface parameter of trioxane made it necessary to reevaluate not only the vapor–liquid equilibrium measurements for methanol/trioxane, but also those for water/trioxane. As the quality of the published vapor–liquid equilibrium data for the water/trioxane system (Kovac and Ziak, 1970; Serebrennaya and Byk, 1966) is rather poor, new measurements were carried out. The results are given in the Tables 5a and 5b.

The binary parameters for interactions between trioxane as one component and water or methanol as the second one were

Table 9. (Continued)

$\tilde{y}_{Me}$			$\tilde{y}_{Tri}$			p		
Exp.	Calc.	100 D	Exp.	Calc.	100 D	Exp.	Calc.	100 D
mol/mol			mol/mol			kPa		
0.110	0.121	10.4	0.072	0.075	5.2	36.32	37.26	2.6
0.088	0.097	9.5	0.080	0.083	4.4	37.56	36.79	−2.0
0.081	0.079	−2.4	0.073	0.074	0.8	36.70	35.77	−2.5
0.831	0.840	1.0	0.033	0.032	−3.7	99.50	97.89	−1.6
0.193	0.244	26.0	0.031	0.032	3.2	41.13	40.73	−1.0
0.630	0.661	4.8	0.039	0.034	−11.1	76.45	73.66	−3.7
0.816	0.841	3.1	0.050	0.049	−2.2	99.53	98.90	−0.6
0.765	0.791	3.5	0.076	0.067	−11.4	92.34	93.33	1.1
0.731	0.737	0.9	0.017	0.015	−12.6	87.22	81.03	−7.1
0.077	0.090	16.2	0.024	0.030	21.9	34.10	34.10	0.0
0.046	0.049	7.7	0.036	0.044	23.0	33.25	33.40	0.4
0.188	0.216	14.9	0.087	0.079	−9.9	40.66	41.18	1.3
0.752	0.789	5.1	0.069	0.065	−6.5	93.05	91.90	−1.2
0.742	0.719	−3.1	0.023	0.020	−15.5	78.82	78.12	−0.9
0.787	0.790	0.4	0.036	0.032	−9.6	89.73	88.59	−1.3
0.256	0.291	13.5	0.064	0.057	−10.9	43.11	43.68	1.3
0.816	0.841	3.0	0.016	0.014	−11.0	93.65	92.97	−0.7
0.080	0.094	18.0	0.082	0.081	−1.2	36.46	35.96	−1.4
0.175	0.212	20.8	0.095	0.089	−6.9	40.66	40.93	0.7
0.110	0.118	6.5	0.061	0.058	−5.8	36.31	36.15	−0.4
0.516	0.592	14.6	0.027	0.025	−6.3	59.88	62.62	4.6
0.768	0.789	2.8	0.039	0.037	−6.0	83.79	84.96	1.4
0.259	0.305	17.4	0.055	0.051	−8.0	42.20	43.10	2.1
0.138	0.136	−1.6	0.106	0.094	−10.7	37.77	37.44	−0.9
0.375	0.407	8.7	0.031	0.027	−12.1	47.23	47.25	0.0
0.194	0.235	20.7	0.045	0.040	−9.8	38.04	38.64	1.6
0.764	0.782	2.5	0.018	0.017	−4.8	77.92	78.16	0.3
0.676	0.711	5.3	0.053	0.052	−3.3	70.51	71.28	1.1
0.770	0.746	−3.1	0.086	0.081	−6.7	74.62	74.66	0.0
0.848	0.853	0.7	0.018	0.018	−4.4	82.34	84.08	2.1
0.665	0.664	−0.4	0.095	0.086	−9.4	66.17	66.90	1.1
0.803	0.811	0.9	0.018	0.017	−4.0	78.23	78.65	0.5
0.792	0.775	−2.1	0.056	0.053	−6.2	75.80	76.45	0.9
0.780	0.804	3.1	0.020	0.020	−1.2	72.48	73.37	1.2
0.127	0.150	18.3	0.058	0.060	4.7	86.73	86.00	−0.8
0.124	0.119	−3.4	0.054	0.039	−26.6	82.29	82.13	−0.2
0.185	0.196	5.8	0.031	0.029	−6.9	88.86	87.52	−1.5
0.095	0.111	16.0	0.075	0.079	5.8	90.90	84.72	−6.8
0.241	0.253	4.9	0.039	0.037	−5.8	92.80	93.22	0.5
0.072	0.074	3.8	0.073	0.069	−5.0	87.19	81.10	−7.0
0.085	0.078	−8.8	0.048	0.044	−6.9	80.64	79.40	−1.5
0.104	0.103	−1.2	0.051	0.049	−3.4	82.19	80.82	−1.7
0.210	0.224	6.8	0.040	0.038	−5.4	88.94	89.05	0.1
0.245	0.265	8.3	0.048	0.045	−4.6	93.22	93.51	0.3
0.079	0.069	−12.7	0.047	0.046	−1.1	79.09	77.81	−1.6
0.257	0.284	10.5	0.059	0.060	1.7	93.77	94.47	0.7
0.063	0.064	2.1	0.070	0.072	2.6	84.26	78.67	−6.6
0.235	0.279	18.9	0.065	0.072	9.8	91.37	92.48	1.2
0.171	0.192	12.4	0.076	0.084	10.6	85.54	85.47	−0.1
	6.3			−3.7			−0.5	
	8.2			8.6			2.4	

now preferentially fitted to low concentration data, e.g., the results for strongly diluted trioxane solutions. Thus, a better representation of the data in the diluted regions is achieved. However, somewhat larger deviations in the industrially less important intermediate concentration range have to be accepted. The final parameters are given in Table 6. A comparison of the experimental data for the methanol/trioxane and the water/trioxane system with the correlation is shown in Figures 3 and 4.

With the new parameters, the predictions of vapor–liquid equilibria in the ternary system, water/methanol/trioxane, are considerably improved. The predictions for the multicomponent formaldehyde- and trioxane-containing systems are strongly

affected, but the improvements are not essential, because the model for aqueous and methanolic formaldehyde solutions of trioxane is very sensitive to parameters describing the physical interactions between trioxane and formaldehyde polymers. As these polymers are unstable as pure substances, their binary systems with trioxane cannot be investigated experimentally. Therefore, the ternary data had to be used to determine these interactions more accurately. Essential progress could be achieved by fitting parameters for interactions between trioxane on one side and $HO(CH_2O)H$ and CH_2OH on the other side, to experimental data for the formaldehyde/water/trioxane system (Maurer, 1986) and for the formaldehyde/methanol/trioxane system (Table 7).

Table 6 gives the complete set of UNIFAC parameters for interactions between trioxane and other groups, recommended for use in calculations of vapor–liquid equilibria in aqueous and methanolic solutions containing formaldehyde and trioxane. All other parameters needed for the calculations can be taken from the original work of Maurer (1986), as the revision and extension only considers trioxane-containing systems.

Vapor–liquid equilibria in industrially important, multicomponent, formaldehyde- and trioxane-containing mixtures, such as low-concentration solutions of trioxane, are well described and predicted by the model with the new parameters. (A FORTRAN 77 program for vapor–liquid equilibrium calculations in formaldehyde-containing multicomponent mixtures is available from the authors on request.) This can be seen from Tables 7–9, where new experimental data are presented together with calculated data. For all calculations, the liquid-phase concentration and the property given in the first column (either temperature or pressure) were preset and all other properties calculated. Only in some cases, the deviations between calculated and measured gas-phase concentrations are considerably larger than the experimental uncertainties.

Summary

Aqueous and methanolic formaldehyde solutions are examples of complex mixtures. The complexity arises from chemical reactions, as formaldehyde is dissolved predominantly in the form of different polymers. Therefore, chemical reactions and intermolecular forces have to be taken into consideration for the description of vapor–liquid equilibria in these systems. This becomes evident when chemically inert substances like trioxane, which exhibit strong intermolecular forces with the solvents, are added. It is shown that a recently published physico-chemical vapor–liquid equilibrium model for aqueous and methanolic formaldehyde solutions (Maurer, 1986) can be successfully extended to include such inert components, but the estimation of unavoidable additional parameters is essential for the model performance. The procedure described here for trioxane-containing formaldehyde solutions might be an example that can be used for extensions to other industrially important substances.

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Notation

a = UNIFAC interaction parameter
$D = (z^{exp} - z^{calc})/z^{exp}$
$\bar{D} = (\sum_{i=1}^{N} D_i)/N$
FA = formaldehyde
HF = hemiformal
HF_n = polyoxymethylene hemiformal (n = number of CH_2O groups)
K = chemical reaction constant
Me = methanol
MG = methylene glycol
MG_n = polyoxymethylene glycol (n = number of CH_2O groups)
N = number of experimental points
p = pressure
p^{θ} = standard state pressure (1 atm)
p^s = vapor pressure
q = UNIFAC surface parameter
r = UNIFAC size parameter
$S_D = \sqrt{[\sum_{i=1}^{N} (D_i - \bar{D})^2]/(N-1)}$
T = temperature
Tri = trioxane
W = water
x = liquid-phase mole fraction
$\tilde{x}$ = overall liquid-phase mole fraction
y = gas-phase mole fraction
$\tilde{y}$ = overall gas-phase mole fraction
z = miscellaneous property
γ = activity coefficient, normalized corresponding to Raoult's law

Literature Cited

Brandani, V., and G. Di Giacomo, "Effect of Small Amounts of Methanol on the Vapor–Liquid Equilibrium for the Water-Formaldehyde System," *Fluid Phase Equilib.*, **24**, 307 (1985).

Brandani, V., G. Di Giacomo, and P. U. Foscolo, "Isothermal Vapor–Liquid Equilibria for the Water-Formaldehyde System: a Predictive Thermodynamic Model," *Ind. Eng. Chem. Proc. Des. Dev.*, **19**, 179 (1980).

———, "Thermodinamica delle Soluzioni Acquose di Formaldeide: Equilibri in Fase Liquida," *La Chimica e l'Industria*, **58**, 99 (1976).

Brandani, V., G. Di Giacomo, and V. Mucciante, "Vapor–Liquid Equilibrium of Formaldehyde-Water-Methanol Mixtures," *La Chimica e l'Industria*, **69**, 9 (1987).

Gmehling, J., P. Rasmussen, and A. Fredenslund, "Vapor–Liquid Equilibria by UNIFAC Group Contribution: 2. Revision and Extension," *Ind. Eng. Chem. Proc. Des. Dev.*, **21**, 118 (1982).

Hasse, H., "Dampf-Flüssigkeits-Gleichgewichte, Enthalpien und Reaktionskinetik in Formaldehydhaltigen Mischungen," PhD Thesis, Universität Kaiserslautern (1990).

Kogan, L. V., "Mathematical Description of Phase Behavior of Systems Whose Components Enter into Polymerization Reactions," *Zhur. Prikl. Khim.*, **52**, 2149 (1979).

Kogan, L. V., and S. K. Ogorodnikov, "Liquid–Vapor Equilibrium in the System Formaldehyde-Methanol-Water," *Zhur. Prikl. Khim.*, **53**, 119 (1980).

Kovac, A., and J. Ziak, "Rovnovaka Kvapalinia Para Sustavy Trioxan-Voda," *Petrochemia 10*, **2**, 77 (1970).

Maurer, G., "Vapor–Liquid Equilibrium of Formaldehyde- and Water-Containing Multicomponent Mixtures," *AIChE J.*, **32**, 932 (1986).

Prausnitz, J. M., T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1980).

Serebrennaya, I. I., and S. Sh. Byk, "Liquid–Vapor Equilibrium in the System Trioxane/Water under Atmospheric Pressure," *Zhur. Prikl, Khim.*, **39**, 1869 (1966).

Tunik, S. P., O. A. Larova, and T. M. Lesteva, "Liquid–Vapor-Phase Equilibria in Formaldehyde-Water-Alcohol Systems: II. a Method for the Interpretation of Liquid–Vapor Equilibrium Data for the Methanol Formaldehyde Water System with a Chemical Reaction," *Zhur. Fiz. Khim.*, **51**, 2707 (1977).

Ullmann's Encyclopedia of Industrial Chemistry, Vol. A, Alphabetically Arranged Articles, 11 Fibers, Synthetic Inorganic to Formaldehyde, 5th comp. rev. ed., VCH Weinheim (1988).

Walker, J. F., *Formaldehyde*, ACS Monograph, 3rd ed., Reinhold, New York (1964).

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