Vapor-Liquid and Chemical Equilibria of Formaldehyde-Water Mixtures

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A physicochemical model of the thermodynamic properties of formaldehyde-containing mixtures was revised and extended using new experimental data for vapor−liquid and chemical equilibria. The new vapor−liquid equilibrium data of the formaldehyde−water system were taken for very diluted (formaldehyde concentrations as low as 0.07 mass %) and very concentrated (up to 71 mass %) formaldehyde solutions at temperatures between 363 and 423 K and pressures up to about 650 kPa. The new chemical equilibrium data were obtained applying ^{13}C-NMR spectroscopy to the same system at temperatures between 338 and 383 K at formaldehyde concentrations of up to about 62 mass %. Results from both investigations were used simultaneously—together with data from the literature—to improve a physicochemical model of the thermodynamic properties of aqueous solutions of formaldehyde.

Introduction

Formaldehyde (FA) is a very important chemical intermediate with many uses in the chemical industry. For example, formaldehyde is needed for the production of 1,4-butanediol, urotropine (hexamethylenetetramine), and polyacetal plastics [c.f. Walker (1964)]. Formaldehyde is highly reactive and therefore commonly handled in aqueous and/or methanolic solutions, where it forms different adducts with the solvents. Such mixtures are often processed by distillation and absorption/desorption. The basic design of such processes requires models of the phase equilibrium of aqueous and methanolic formaldehyde mixtures. Such models have to consider not only differences in intermolecular forces but also a variety of chemical reactions.

In aqueous solutions, the most important chemical-reaction products are methylene glycol ($HOCH_2OH$; here, also, MG) and poly(oxymethylene) glycols ($HO(CH_2O)_iH$, $i>1$; here, also, MG_i):

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

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

These chemical reactions have an essential influence on the properties of formaldehyde-containing solutions and they have to be taken into account in any thermodynamic model of these systems. A physicochemical model, originally developed by Maurer (1986), that combines these chemical reactions with physical interactions, has been proved to be very successful in describing vapor−liquid equilibria and enthalpies in formaldehyde-containing mixtures. This model has been continuously updated [see, for example, Hahnenstein et al. (1994b) for a survey up to 1992], and its application range was extended as new, reliable data became available.

The equilibrium distribution of formaldehyde to its reaction products with water (W) has an essential influence not only on equilibrium properties, but also on chemical-reaction kinetics and transport properties. Information on that equilibrium distribution is accessible from spectroscopic investigations. Such investigations reveal that in aqueous solutions

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formaldehyde is predominantly present as methylene glycol and poly(oxymethylene) glycols, but rarely as free, molecular formaldehyde. Using a high-resonance-frequency nuclear-magnetic-resonance (NMR) spectrometer, it is possible to separate signals from $-CH_2-$ groups in different poly(oxymethylene) glycols [c.f. Le Botlan et al. (1983)]. That technique is suitable for investigating the polymerization reactions (II). Such studies were carried out for the determination of both equilibrium properties and chemical-reaction kinetic properties [for a survey of literature data on (a) equilibrium properties, see, for example, Hahnenstein et al. (1994a) and Balashov et al. (1996); (b) on reaction kinetics see Hahnenstein et al. (1995)]. However, spectroscopic investigations give only information on species concentrations, whereas in thermodynamic calculations the activities or activity coefficients have to be known. In a recently published update of the model of Maurer (1986) by Albert et al. (1996) it was assumed that activity coefficients have only to be taken into account for the description of the phase equilibrium whereas their influence on the chemical-reaction equilibria can be neglected, that is, true thermodynamic chemical reaction constants K_a were approximated by K_x:

$$K_{a,MG_i} = \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}} \cdot \frac{\gamma_{MG_i} \cdot \gamma_W}{\gamma_{MG_{i-1}} \cdot \gamma_{MG}} \approx \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}} = K_{x,MG_i} \quad \text{for all } i > 1. \quad (1)$$

That model was successfully applied to describe the vapor–liquid equilibrium in aqueous solutions of formaldehyde. It also enabled a straightforward extension to describe chemical reaction and transport kinetics in such solutions.

However, the description of the chemical-reaction equilibrium conditions with equilibrium constants K_x rather than with thermodynamic equilibrium constants K_a introduced an inconsistency in the model. In recent applications (Ross, private communication, 1997), that deficiency caused problems, especially when the model was applied to concentrated solutions where differences between compositions and activities become larger. For example, the description of the azeotrope with that model presents problems because the maximum value for the pressure (for constant temperature) was not reached in the azeotropic point.

Furthermore, there is a great deal of interest from industry in extending the model to higher temperatures, a higher formaldehyde concentration (close to the concentrations where solid paraformaldehyde precipitates), as well as to check the model performance at very small formaldehyde concentrations. Therefore, the present work was to extend the model into those regions as well as to (again) incorporate ''true'' thermodynamic chemical equilibria. That extension was achieved by including new experimental data for the species distribution at higher formaldehyde concentrations and new experimental data for the vapor–liquid equilibrium (particularly at higher temperatures and at very small as well as at very high formaldehyde concentrations) while updating the model.

While in previous work model parameters were fitted to phase-equilibrium data and experimental results for ''pseudo''-chemical-reaction equilibrium constants K_x determined from NMR spectroscopy, a somewhat different approach was applied here, as model parameters were fitted to experimental data for the phase equilibrium and the distribution of formaldehyde to poly(oxymethylene) glycols. Thus, the intermediate step of introducing pseudoconstants K_x was avoided.

The updated model gives a good representation of vapor–liquid equilibrium data in binary systems of formaldehyde and water over the entire composition and temperature ranges where reliable experimental data are available. Deviations between measured and calculated values are typically below 5% for the partition coefficient of formaldehyde and 2% for the pressure, in other words, the results are at least as accurate as those obtained with the previous version of that model (Albert et al., 1996). On the other hand, the model covers a wider range of temperature and formaldehyde concentrations. The updated model also gives a reliable description of the NMR data for the concentrations of the poly(oxymethylene) glycols. The relative deviations between the experimental and calculated concentrations are typically below about 6%. Furthermore, the model also reliably predicts the experimental results of Liu et al. (1992) for the enthalpy change encountered in the partial evaporation of aqueous formaldehyde solutions.

Experimental Section

Vapor–liquid equilibrium

Experimental work on the vapor–liquid equilibrium of the formaldehyde–water system was performed at temperatures between 363 and 423 K at very low (≥ 0.07 mass %) as well as at rather high (≤ 71 mass %) formaldehyde concentrations in the liquid, that is, under conditions where no or only very little information on the vapor–liquid equilibrium is available [for a survey on reliable experimental data available in the literature, see Albert et al. (1996)]. The phase-equilibrium apparatus used in the present work was described in detail before [cf. Albert et al. (1996)], therefore only a short description is given here. The central part of the apparatus consists of a thin-film evaporator. There, a rotating coil spreads the thermostated, equilibrated liquid feed on the inner surface of a tube, which is surrounded by a heating jacket. The temperature of that heating jacket is kept at a constant temperature only a few kelvins above that of the feed. The liquid partially evaporates at nearly constant pressure. That pressure is supplied by a backpressure regulator. Experiments are carried out at small evaporation ratios and sufficient residence time, so that the coexisting phases leaving the thin-film evaporator are in chemical as well as in phase equilibrium. The coexisting phases are separated at the thin-film evaporator outlet. The liquid phase is subcooled, and the vapor phase is completely condensed. Both phases are collected in small vials, and the collected samples are analyzed for formaldehyde using the sodium sulfite method (Walker, 1964). Formaldehyde concentrations are determined with a relative error of less than 2%. The temperature and the pressure are measured with an accuracy of ± 0.1 K and ± 0.5 kPa, respectively.

Feed solutions were prepared by dissolving paraformaldehyde (Merck, purity higher than 95%) in bidistilled water at a high temperature, and any solid residue was removed by fil-

Table 1. Experimental Results for the Vapor–Liquid Equilibrium of Formaldehyde + Water at 363 K at Low and High Formaldehyde Concentrations

p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}	p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}
68.9	0.0006	0.0008	71.4	0.1992	0.1682
68.9	0.0029	0.0040	71.0	0.1999	0.1661
68.9	0.0029	0.0038	70.7	0.2074	0.1650
67.6	0.0054	0.0069	71.0	0.2996	0.2197
70.1	0.0054	0.0073	70.7	0.3067	0.2219
70.1	0.0055	0.0068	70.4	0.3367	0.2416
69.3	0.0057	0.0084	69.9	0.3478	0.2434
68.6	0.0109	0.0142	68.7	0.3957	0.2634
70.0	0.0114	0.0158	68.7	0.3983	0.2621
70.3	0.0279	0.0347	67.1	0.4497	0.2977
70.7	0.0280	0.0359	67.3	0.4674	0.2999
69.4	0.0289	0.0355	66.1	0.4882	0.3178
			66.1	0.4883	0.3107
			64.7	0.5897	0.3558
			64.4	0.6040	0.3211

tration (Hasse, 1990). This procedure is suitable for producing solutions of up to about 0.22 mol·mol^{-1} formaldehyde, whereas for higher formaldehyde concentrations, such solutions were concentrated by reflux distillation.

Vapor–liquid equilibrium data in the formaldehyde–water system were measured in the temperature range from 363 K to 423 K at pressures up to 650 kPa. The liquid-phase formaldehyde concentration ranged from 0.04 to 10 mol % (0.07 to 15 mass %) of formaldehyde (low concentration range) and from about 12 to about 60 mol % (18 to 71 mass %) of formaldehyde (high concentration range). The new experimental results are given in Tables 1 to 4.

Chemical equilibrium

The results of NMR–spectroscopic investigations of chemical equilibria in the formaldehyde–water system were recently reported by Hahnenstein et al. (1994a)—for formaldehyde concentrations between 10 and 17 mol % at temperatures between 281 and 358 K—and by Balashov et al. (1996)—for formaldehyde concentrations between 20 and 46 mol % at temperatures between 323 and 368 K. In the present work NMR–spectroscopic investigations were carried out for formaldehyde concentrations in the 6 to 45 mol % range at temperatures between 338 to 383 K. That new experimental material therefore complements recently published data in the literature.

The NMR–spectroscopic experiments were carried out with a Brucker AMX 400 NMR spectrometer (400.13 MHz). The spectrometer is equipped with an internal temperature-control device with an external temperature display. This device was calibrated by investigating the chemical shift of ethylene glycol at different temperatures, while all other variables—for example, flow rate of air used for thermostating the spectrometer, and the speed of rotation of the sample—were kept constant. For this calibration the influence of temperature on the chemical shift of 1,2-ethanediol was taken from Günther (1994). The uncertainty in the measured temperatures is estimated to be about one kelvin.

Formaldehyde solutions were prepared and analyzed as described earlier. The samples were sealed in glass capillaries. Prior to the spectroscopic investigations, the capillaries were kept at the spectrometer temperature in a thermostated bath for several hours to ensure chemical equilibrium. ^{13}C-NMR spectra were taken using benzene-d_6 in sealed capillaries as magnetic field lock and reference substance for the chemical shift. Some spectra were also taken for solutions of formaldehyde in H_2O/D_2O mixtures. As in previous work

Table 2. Experimental Results for the Vapor–Liquid Equilibrium of Formaldehyde + Water at 383 K at Low and High Formaldehyde Concentrations

p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}	p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}
144.3	0.0005	0.0010	156.4	0.2052	0.2287
144.5	0.0005	0.0010	154.3	0.2872	0.2785
143.5	0.0028	0.0051	154.6	0.2899	0.2768
144.4	0.0029	0.0053	155.9	0.3067	0.2716
145.5	0.0052	0.0097	152.7	0.3766	0.3309
144.8	0.0052	0.0098	152.8	0.3785	0.3304
144.9	0.0101	0.0183	151.1	0.5003	0.4031
146.1	0.0107	0.0196	149.9	0.5008	0.4035
146.8	0.0273	0.0450	145.3	0.6035	0.4798
146.8	0.0281	0.0463	145.3	0.6050	0.4829
151.2	0.0934	0.1245			
153.2	0.1003	0.1287			

Table 3. Experimental Results for the Vapor–Liquid Equilibrium for Formaldehyde + Water at 413 K at Low and High Formaldehyde Concentrations

p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}	p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}
363.8	0.0004	0.0011	442.5	0.2751	0.3536
364.1	0.0005	0.0014	442.5	0.2792	0.3498
367.2	0.0026	0.0070	451.7	0.3730	0.4256
368.0	0.0048	0.0127	452.0	0.3743	0.4224
368.0	0.0049	0.0125	457.0	0.4823	0.5040
368.9	0.0049	0.0137	456.1	0.4862	0.4994
370.3	0.0051	0.0141	450.9	0.6049	0.5934
371.3	0.0096	0.0260			
374.1	0.0103	0.0281			
379.7	0.0212	0.0544			
383.7	0.0251	0.0609			
404.9	0.0720	0.1478			
406.8	0.0730	0.1474			

Table 4. Experimental Results for the Vapor–Liquid Equilibrium of Formaldehyde + Water at 423 K at Low and High Formaldehyde Concentrations

p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}	p kPa	$\tilde{x}_{FA}$ mol·mol^{-1}	$\tilde{y}_{FA}$ mol·mol^{-1}
479.9	0.0004	0.0013	560.2	0.1211	0.2314
484.0	0.0025	0.0074	560.2	0.1225	0.2297
485.1	0.0027	0.0077	588.3	0.1969	0.3066
485.6	0.0043	0.0133	588.6	0.1980	0.3082
486.9	0.0045	0.0143	608.5	0.2728	0.3679
494.1	0.0099	0.0296	608.6	0.2750	0.3713
493.8	0.0101	0.0302	625.1	0.3605	0.4405
508.0	0.0243	0.0666	623.7	0.3703	0.4444
508.3	0.0244	0.0678	639.8	0.4717	0.5226
			639.7	0.4786	0.5169
			645.6	0.5948	0.6251

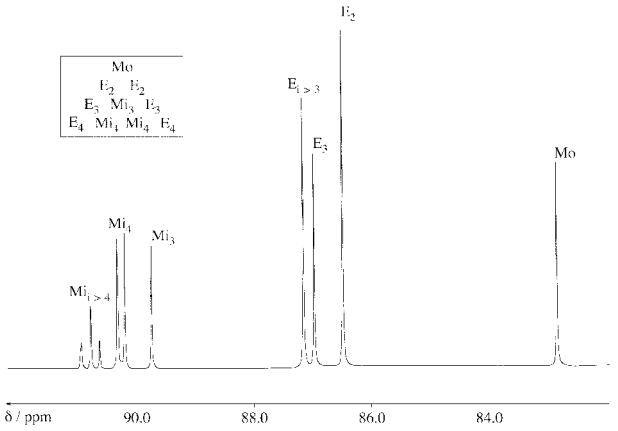

Figure 1. ^{13}C-NMR spectrum of a formaldehyde–water solution at 338 K and $\tilde{x}_{FA} = 0.446$ mol·mol^{-1}.

(cf. Hahnenstein et al., 1994a; Balashov et al., 1996), substituting heavy water for water did not result in any detectable shift in the composition of the formaldehyde solution. The assignment of the peaks to the different $-CH_2-$ groups in methylene glycol and poly(oxymethylene) glycols was adopted from earlier work (Hahnenstein et al., 1994a; Balashov et al., 1996), and is given in Figure 1, which shows a ^{13}C-NMR spectrum of an aqueous solution containing about 45 mol % of formaldehyde at 338 K. The base line was very stable in all experiments and, at high formaldehyde concentrations, the peak areas could be reproduced within about 1%. For diluted formaldehyde solutions, however, the peak areas were rather small and the reproducibility decreased, especially for peaks due to $-CH_2-$ groups in higher poly(oxymethylene) glycols. The peak areas were converted into concentrations, assuming that the peak areas are proportional to the number of the corresponding groups and that the constant of proportionality is the same for all NMR-active $-CH_2-$ groups. However, because there is neither a peak due to monomeric formaldehyde nor is it possible to distinguish between the peaks caused by poly(oxymethylene) glycols containing more than four formaldehyde monomers, some additional assumptions are required for qualitatively assessing the peak areas of the formaldehyde oligomer concentrations. The pseudo-chemical-equilibrium constant for the formation of methylene glycol [cf. reaction (I)] given by Siling and Akselrod (1968) was used to calculate the (very small) concentration of monomeric formaldehyde from the NMR results for the concentration of methylene glycol. Because the amount of monomeric formaldehyde in the liquid phase is always very small, the uncertainty in the mass balance of formaldehyde caused by that approximation was neglected. The concentrations of all poly(oxymethylene) glycols containing more than four formaldehyde molecules were estimated, assuming that, at a constant temperature and constant overall mole fraction of formaldehyde, the pseudo-chemical-equilibrium constant

$$K_{x,MG_i} = \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}} \qquad (2)$$

is constant for $i > 3$.

Table 5. NMR–Spectroscopic Data for the Species Distribution of Liquid Mixtures of Formaldehyde + Water

T K	$\tilde{x}_{FA}$ mol·mol^{-1}	x_W	x_{MG}	x_{MG_2}	x_{MG_3}	x_{MG_4}
		mol·mol^{-1}				
338.15	0.0605	0.9482	0.0409	0.0091	0.0014	0.0002
	0.1295	0.8987	0.0657	0.0261	0.0068	0.0017
	0.2049	0.8525	0.0783	0.0429	0.0161	0.0061
	0.2779	0.8027	0.0911	0.0595	0.0260	0.0113
	0.3851	0.7310	0.1009	0.0785	0.0417	0.0221
	0.4460	0.6922	0.0992	0.0870	0.0506	0.0294
353.15	0.0605	0.9474	0.0422	0.0086	0.0013	0.0002
	0.1295	0.8961	0.0695	0.0254	0.0063	0.0016
	0.1888	0.8575	0.0811	0.0409	0.0134	0.0044
	0.2049	0.8496	0.0824	0.0423	0.0157	0.0058
	0.2132	0.8437	0.0840	0.0447	0.0168	0.0063
	0.2779	0.8022	0.0930	0.0578	0.0257	0.0114
	0.2910	0.7944	0.0930	0.0612	0.0277	0.0126
	0.3475	0.7544	0.1009	0.0721	0.0359	0.0179
	0.3851	0.7315	0.1001	0.0785	0.0417	0.0222
	0.4460	0.6902	0.1010	0.0873	0.0506	0.0294
368.15	0.0605	0.9466	0.0432	0.0087	0.0010	0.0001
	0.1295	0.8962	0.0695	0.0250	0.0064	0.0016
	0.1888	0.8557	0.0847	0.0390	0.0131	0.0044
	0.2049	0.8452	0.0871	0.0434	0.0152	0.0053
	0.2132	0.8406	0.0888	0.0435	0.0163	0.0061
	0.2779	0.8011	0.0947	0.0573	0.0255	0.0113
	0.2910	0.7917	0.0972	0.0600	0.0273	0.0124
	0.3475	0.7555	0.1011	0.0703	0.0355	0.0180
	0.3851	0.7298	0.1019	0.0786	0.0416	0.0220
	0.4460	0.6878	0.1035	0.0874	0.0506	0.0292
383.15	0.0605	0.9478	0.0419	0.0077	0.0016	0.0003
	0.0605	0.9468	0.0432	0.0080	0.0012	0.0002
	0.1295	0.8954	0.0707	0.0246	0.0062	0.0016
	0.1295	0.8930	0.0733	0.0256	0.0055	0.0012
	0.2049	0.8473	0.0854	0.0418	0.0154	0.0057
	0.2779	0.7969	0.0981	0.0591	0.0254	0.0109
	0.3851	0.7253	0.1041	0.0814	0.0422	0.0218
	0.4460	0.6862	0.1051	0.0873	0.0505	0.0292

Thus the experimental results for the peak areas were used to determine (at constant temperature and constant concentration of formaldehyde) two pseudo-chemical-equilibrium constants (K_{x,MG_2} and K_{x,MG_3}). A maximum-likelihood procedure was applied to take the uncertainty of the peak areas into account in the determination of those pseudoconstants. From the pseudoconstants the concentrations of water, methylene glycol, and the oligomers containing up to four formaldehyde monomers were calculated. They are given in Table 5. The concentrations of all higher formaldehyde oligomers can be calculated by applying Eq. 2 using numbers for K_{x,MG_i}, as determined from the concentrations of water, methylene glycol, and the poly(oxymethylene) glycols containing 3 and 4 formaldehyde monomers, as given in Table 5.

The previously unpublished results of the NMR–spectroscopic investigations by Hahnenstein et al. (1994a) were treated in the same way as the new experimental data. The results are given in Table 6.

Model

Different models have been proposed to describe the vapor–liquid equilibrium in the formaldehyde–water system (c.f., Albert et al., 1996, for a short overview). The model

Table 6. NMR–Spectroscopic Data for the Species Distributions of Liquid Mixtures of Formaldehyde + Water (Evaluation of Spectroscopic Data of Hahnenstein et al. (1994a))

T	$\tilde{x}_{FA}$	x_W	x_{MG}	x_{MG_2}	x_{MG_3}	x_{MG_4}
K	mol·mol^{-1}	mol·mol^{-1}				
281.65	0.0940	0.9267	0.0493	0.0186	0.0044	0.0011
280.60	0.1270	0.9050	0.0578	0.0265	0.0081	0.0026
283.80	0.1670	0.8802	0.0639	0.0366	0.0136	0.0056
298.15	0.0940	0.9256	0.0509	0.0185	0.0040	0.0009
297.85	0.1270	0.9026	0.0610	0.0269	0.0074	0.0021
299.75	0.1670	0.8786	0.0663	0.0365	0.0133	0.0053
317.15	0.0940	0.9236	0.0544	0.0175	0.0037	0.0008
317.01	0.1270	0.9008	0.0638	0.0264	0.0070	0.0020
317.68	0.1670	0.8767	0.0690	0.0363	0.0129	0.0050
337.15	0.0590	0.9494	0.0397	0.0097	0.0012	—
337.15	0.0940	0.9213	0.0575	0.0175	0.0038	—
337.20	0.1270	0.8981	0.0682	0.0256	0.0064	0.0017
336.80	0.1670	0.8736	0.0735	0.0363	0.0119	0.0046
357.15	0.0590	0.9481	0.0423	0.0084	0.0012	—
357.15	0.0940	0.9213	0.0580	0.0166	0.0036	0.0004
357.15	0.1180	0.9064	0.0627	0.0231	0.0060	0.0017
357.15	0.1180	0.9060	0.0635	0.0229	0.0059	0.0017
358.15	0.1600	0.8747	0.0771	0.0345	0.0105	0.0032
357.53	0.1670	0.8700	0.0786	0.0364	0.0109	0.0041

used here follows the outline shown in Figure 2 (Maurer, 1986). It is assumed that the vapor above an aqueous solution of formaldehyde consists of three species: water, formaldehyde monomers, and methylene glycol. These species are also present in the liquid phase. But the liquid also contains higher poly(oxymethylene) glycols. The vapor phase is assumed to behave like a mixture of ideal gases, but the chemical-reaction equilibrium for the formation of methylene glycol from formaldehyde and water is taken into account through the chemical-reaction equilibrium constant

$$K^V_{MG}(T) = \frac{y_{MG}}{y_{FA} \cdot y_W} \cdot \frac{p^\theta}{p}. \tag{3}$$

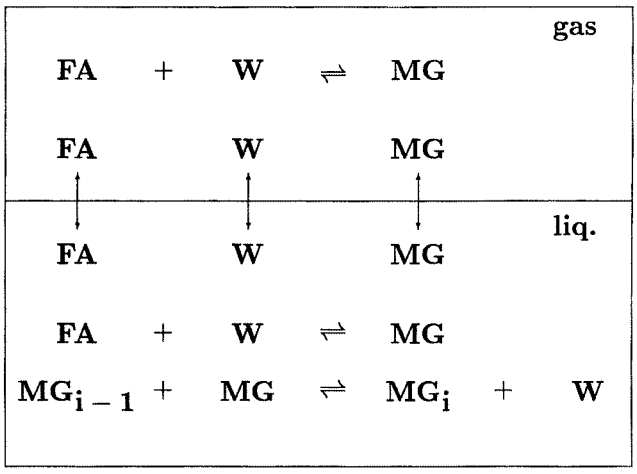

Figure 2. Vapor–liquid equilibrium model for the formaldehyde–water system.

The liquid phase is treated as a real, chemical reactive mixture of water formaldehyde monomers, methylene glycol, and poly(oxymethylene) glycols. The chemical potential of a component in the liquid phase is normalized according to Raoult's law. The nonideality of the liquid phase is taken into account by applying the UNIFAC group contribution method (Fredenslund et al., 1977). Chemicalreaction equilibria are taken into account through true reaction equilibrium constants, that is, those expressed using activities:

$$K_{a,MG} = \frac{x_{MG}}{x_{FA} \cdot x_W} \cdot \frac{\gamma_{MG}}{\gamma_{FA} \cdot \gamma_W} = K^V_{MG}(T) \frac{p^s_{FA} \cdot p^s_W}{p^s_{MG} \cdot p^\theta} \tag{4}$$

$$K_{a,MG_i} = \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}} \cdot \frac{\gamma_{MG_i} \cdot \gamma_W}{\gamma_{MG_{i-1}} \cdot \gamma_{MG}}; \qquad i \geq 2. \tag{5}$$

The vapor–liquid equilibrium is described by extended Raoult's law:

$$p^s_i \cdot x_i \cdot \gamma_i = p \cdot y_i. \tag{6}$$

The chemical reaction equilibria and the phase equilibrium relations are combined with the mass balance for the liquid and the vapor phases:

$$\tilde{x}_{FA} = s \cdot \left(x_{FA} + x_{MG} + \sum_{i=2}^{\infty} i \cdot x_{MG_i} \right) \tag{7}$$

$$\tilde{x}_W = s \cdot \left(x_W + x_{MG} + \sum_{i=2}^{\infty} x_{MG_i} \right), \tag{8}$$

where

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

One of the most essential features of that model is the possibility that it can be extended to include other chemical reactive components, such as, methanol, as well as nonreactive, that is, chemical inert components, such as, trioxane and methylal.

For calculating the vapor–liquid equilibrium in the formaldehyde–water system, the following information is necessary:

- Vapor pressures of pure components, water, formaldehyde, and methylene glycol
- Chemical-reaction equilibrium constants for the formation of methylene glycol in the vapor phase (K^V_{MG}) and the formation of poly(oxymethylene) glycols in the liquid phase ($K_{a,MG}$ and K_{a,MG_i})
- UNIFAC parameters (for size and surface, as well as binary parameters for interactions between all groups).

A complete set of parameters was published along with this model (Maurer, 1986). This model has been continuously updated and extended using new experimental data [cf. Hahnenstein et al. (1994b) for a survey]. In the work of Albert et al. (1996), the model structure was changed in order to re-

Table 7. Pure-Component Vapor Pressure*

Component	*A*	*B*	*C*
Formaldehyde	14.4625	−2,204.13	−30.15
Water	16.2886	−3,816.44	−46.13
Methylene glycol	19.5527	−6,189.19	−9.15

*$\ln \frac{p^S}{\text{kPa}} = A + \frac{B}{T/\text{K} + C}$

duce the calculation time, as well as to include an easy extension to the nonequilibrium effects (transport and reaction kinetics).

The main feature of those changes consisted of assuming that the chemical equilibria may be approximated using equilibrium constants based on mole fractions instead of activities. That assumption resulted, for example, in a considerable reduction in computing time for the sake of introducing some thermodynamic inconsistencies. These inconsistencies are particularly evident when the model is used to calculate azeotropic points. Due to the lack of thermodynamic consistency, the calculated maximum pressure on an isothermal pressure vs. concentration diagram of the binary formaldehyde–water system does not agree with the pressure where the boiling point line touches the dewpoint line. Therefore, in the present work the ''old'' consistent thermodynamic model is used. However, some model parameters are adjusted so that the model also reliably represents the new experimental data.

The equations for the vapor pressures of formaldehyde and water were adopted from earlier versions of the model (Maurer, 1986; Albert et al., 1996). They are given in Table 7. The chemical equilibrium constant (Table 8) for the formation of methylene glycol from water and monomeric formaldehyde in the vapor phase, $K^V_{MG}(T)$, was taken from Kogan (1979b). The chemical equilibrium constant for that chemical reaction in the liquid phase, $K_{a,MG}$, follows from K^V_{MG} (cf. Eq. 4). The division of components into UNIFAC groups (Table 9) is the same as in the original model version (Maurer, 1986). All size and surface parameters for those groups (Table 10) were also taken from earlier work (Maurer, 1986). Some UNIFAC interaction parameters were adopted from the previous model (Maurer, 1986) (cf. Table 11), while others were refitted here. As was shown by Albert et al. (1996), the limiting partition coefficient of formaldehyde in an aqueous solution can be expressed as:

$$\lim_{\tilde{x}_{FA} \to 0} \left(\frac{\tilde{y}}{\tilde{x}} \right)_{FA} = \frac{p^s_{MG}}{p^s_W} \cdot \gamma^{\infty}_{MG,W} \left(1 + \frac{p^{\theta}}{p^s_W \cdot K^V_{MG}} \right). \quad (9)$$

That relation reveals that at small formaldehyde concentrations (that is, when formaldehyde is almost completely converted to methylene glycol), the (unknown) vapor pressure of methylene glycol and the (equally unknown) UNIFAC parameters for interactions between water and methylene glycol are the most important model parameters. Thus, in a first step, these UNIFAC interaction parameters and the vapor pressure of methylene glycol were fitted to experimental vapor–liquid equilibrium data at low formaldehyde concentrations. However, that procedure does not give a unique set of parameters. Therefore, only those data sets were considered further that fulfilled the requirement that the vapor pressure and the enthalpy of vaporization of methylene glycol are consistent with those data for other diols (cf., Maurer, 1986). The remaining parameter sets were then tested in the second step, where all experimental data for the vapor–liquid equilibrium (used by Albert et al., 1996, as well as the new data of this work) and the composition of the liquid phase determined by NMR–spectroscopy, were used to fit the still unknown parameters: two chemical equilibrium constants K_{a,MG_2} and K_{a,MG_i} [for $i > 2$, that is, it was assumed that for $i > 2$ the chemical equilibrium constant does not depend on the number i of formaldehyde monomers in an poly(oxymethylene) glycol MG_i] and the UNIFAC parameters for interactions between the $-CH_2O-$ group and water as well as methylene glycol (that is, a_{12}, a_{21}, a_{13}, and a_{31}), and for interactions between water and methylene glycol (that is, a_{23} and a_{32}). The final results are given in Table 7 (vapor pressure of methylene glycol), Table 8 (chemical equilibrium constants), and Table 11 (UNIFAC interaction parameters).

Table 8. Chemical-Reaction Equilibrium Constants*

Equilibrium Constant	*A*	*B*
K_{MG}	-1.698×10^1	5.233×10^3
K_{MG_2}	4.980×10^{-3}	8.695×10^2
K_{MG_i}, $i > 2$	1.908×10^{-2}	5.445×10^2

*$\ln K = A + B/(T/\text{K})$.

Table 9. UNIFAC-Groups of Components in Formaldehyde Solutions

Component	Groups
FA	1 CH_2O
W	1 H_2O
MG	1 $HO(CH_2O)H$
MG_i	$(i-1)$ CH_2O, 2 OH, 1 CH_2 $\quad i \geq 2$

Table 10. 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

Table 11. UNIFAC Interaction Parameters a_{ij}/K

i j	1	2	3	4	5
1	0.0	774.81*	189.21*	237.7	83.36
2	−142.35*	0.0	189.52*	−229.1	300.0
3	59.20*	−191.82*	0.0	−229.1	300.0
4	28.06	353.5	353.5	0.0	156.4
5	251.5	1,318.0	1,318.0	986.5	0.0

*Determined in the present work.

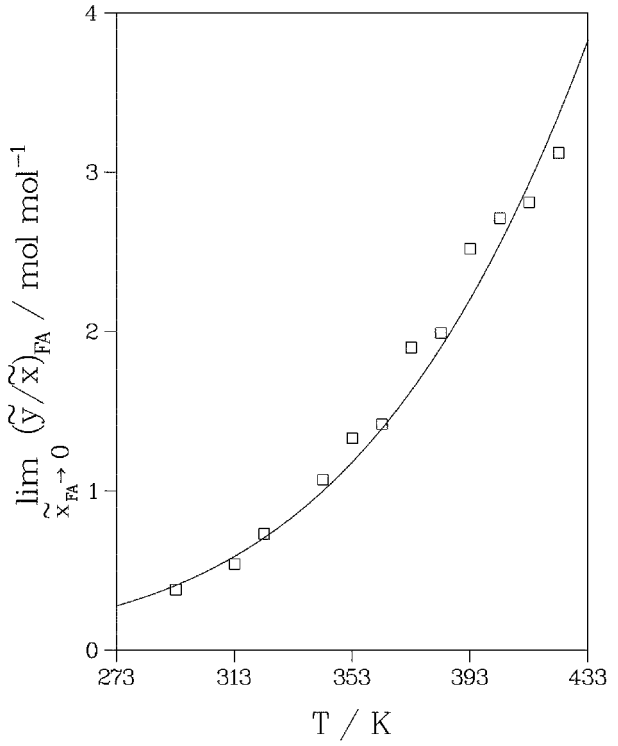

Figure 3. Partition coefficient of formaldehyde at infinite dilution in the formaldehyde–water system.

□, exp. results; ——, corr.

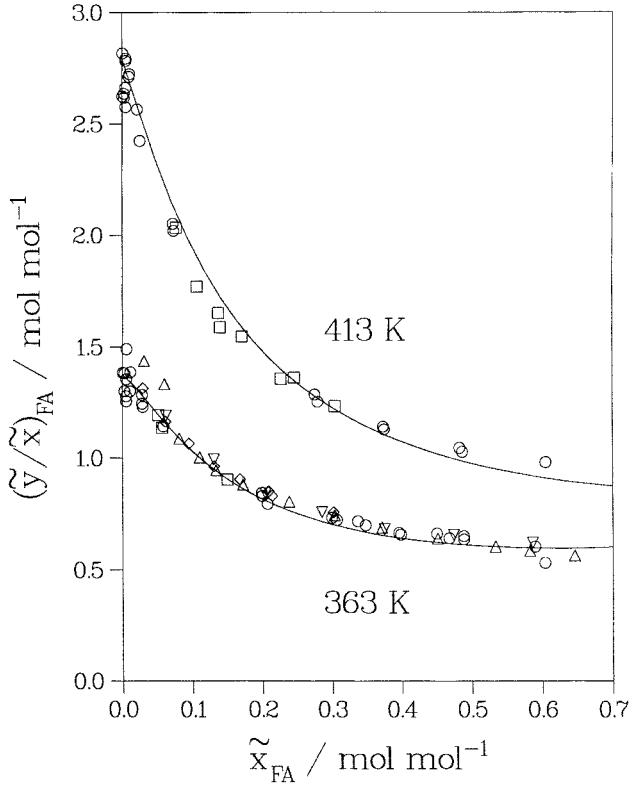

Figure 4. Partition coefficient of formaldehyde in the formaldehyde–water system at 363 K and 413 K.

Exp. Results: ∇, Credali et al. (1965); Δ, Kogan et al. (1977); ◇, Maurer (1986); □ Albert et al. (1996); ○, this work; Corr.—.

Because the model structure is the same as in the original version, the model can be extended easily to include other components, such as, methanol and trioxane.

Comparison with Experimental Results

Vapor–liquid equilibrium

Some typical comparisons between experimental vapor–liquid equilibrium data and calculations from the new model are shown in Figures 3 to 5.

The partition coefficient of formaldehyde at infinite dilution in water is shown in Figure 3. This partition coefficient is defined as the ratio of (overall) mole fractions of formaldehyde in the vapor and liquid phases (cf. also Eq. 9). The relative deviation between calculated and experimental results for that partition coefficient is generally smaller than 5%; the deviation increases to about 10% only for two data points. Figure 4 shows the partition coefficient of formaldehyde as a function of the (overall) liquid-phase formaldehyde mole fraction at 363 and 413 K. The comparison includes not only the new experimental data but also results from the literature (Credali et al., 1965; Kogan et al., 1977; Maurer, 1986; Albert et al., 1996). The calculated partition coefficients agree with the experimental data within the uncertainty of the experimental results of the present work. The partition coefficient of formaldehyde at low formaldehyde concentrations is shown in Figure 5 for 363 and 383 K. This figure proves two statements: first, it confirms the very close agreement between calculated and experimental data (deviations are mostly smaller than 5%), and, second, it shows the relatively small scattering of the experimental results, also at very small formaldehyde concentrations. Similar results were obtained for all other temperatures (cf. Albert, 1999). In general, the new version of the model gives the partition coefficient of formaldehyde in formaldehyde–water solutions within about 5% and the total pressure above those solutions within about 2%.

Chemical equilibrium

Figure 6 shows a comparison between calculated and measured true mole fractions of methylene glycol (MG) and the poly(oxymethylene) glycols containing two (MG_2) and three (MG_3) formaldehyde molecules in an aqueous solution at 338 and 368 K as a function of the overall mole fraction of formaldehyde. That figure confirms that the experimental results reported here are in good agreement with data in the literature (Hahnenstein et al., 1994a; Balashov, 1996). It also shows that at high formaldehyde concentrations the calculated concentrations of MG and MG_2 are systematically above the experimental results. But despite such deviations, the new version of the model agrees much better with the experimental data for the concentration of the formaldehyde oligomers than do the previous ones.

The results shown in Figure 6 are typical for all other temperatures, where reliable NMR data for the species distribu-

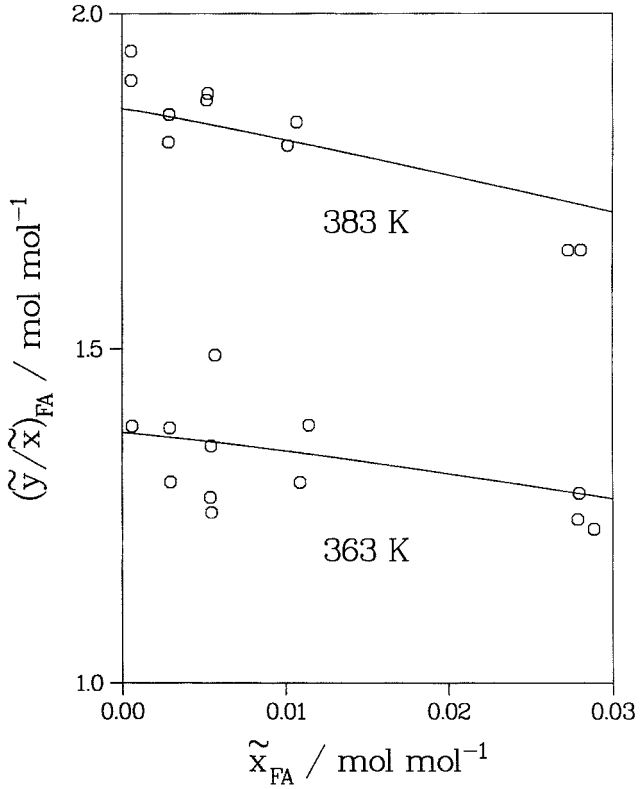

Figure 5. Partition coefficient of formaldehyde at low formaldehyde concentrations in the formaldehyde–water system at 363 K and 383 K: ○, exp. results, this work; ——, corr.

tion in formaldehyde–water solutions is available (cf. Albert, 1999). The influence of temperature on the chemical equilibrium constants, K_{a,MG_2} and K_{a,MG_n} $(n>3)$ (and consequently the enthalpies of reactions), is small. For example, when the temperature is increased from 300 K to 310 K, the relative decrease in K_{MG_2} and K_{MG_n} $(n>3)$ is only 10% and 6%, respectively. The corresponding decrease in the chemical reaction constant, K^V_{MG}, for the formation of methylene glycol in the vapor phase is nearly 60%. Figure 7 shows the comparison between pseudo equilibrium constants K_x for the formation of MG_2 and MG_3 at 353 K, as determined by ^{13}C-NMR spectroscopy in the present work and as calculated from the new version of the model. The figure shows that those pseudoconstants depend on the overall concentration of formaldehyde in the aqueous solution. Again the model reliably describes that influence.

Comparison with calorimetric data

Liu et al. (1992) reported experimental results for the enthalpy change encountered in the partial vaporization of formaldehyde–water solutions. The new version of the model predicts those experimental results for the enthalpy change within about 5%. Thus the new version of the model performs just as well as the previous ones do. The deviations between measured and calculated enthalpy differences encountered in the partial vaporization of formaldehyde–water

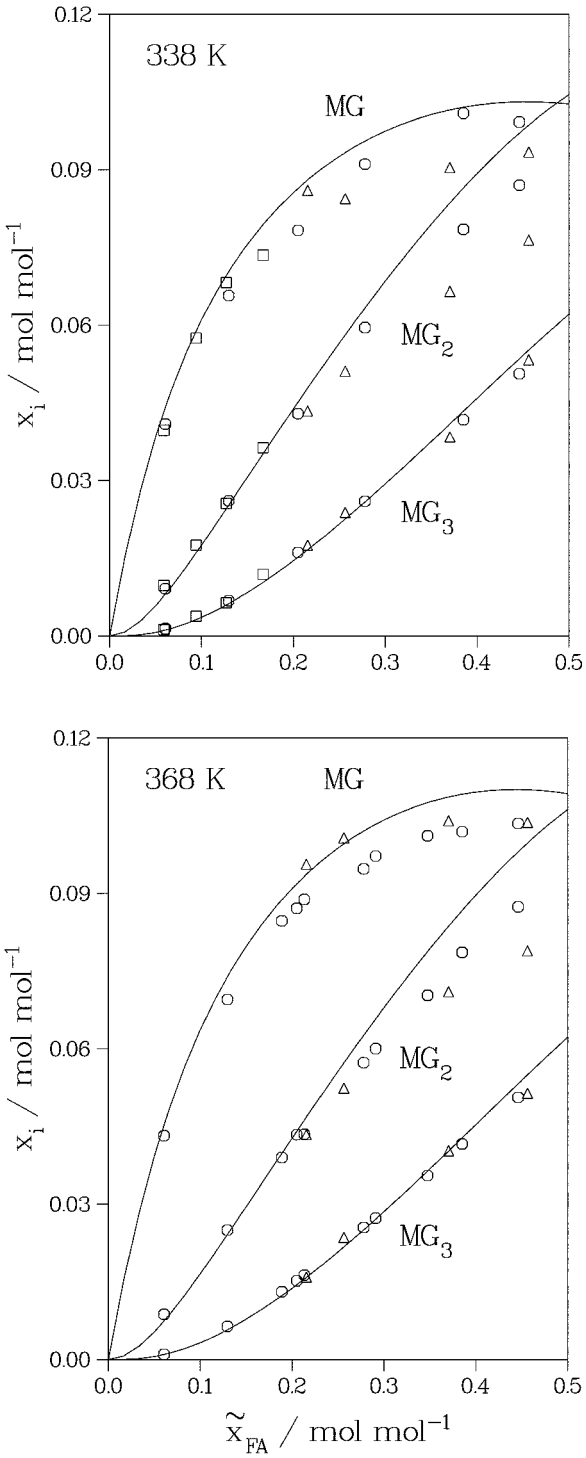

Figure 6. Concentration of methylene glycol (MG) and poly(oxymethylene) glycols MG_2 and MG_3 in chemical equilibria at 338 and 368 K.

Exp. results: ○, Hahnenstein et al. (1994a); □, Balashov et al. (1996); ——, corr. this work.

solutions can be reduced to about 2% by adjusting the chemical reaction enthalpy for the formation of methylene glycol from formaldehyde and water in the vapor phase (cf. Eq. I)

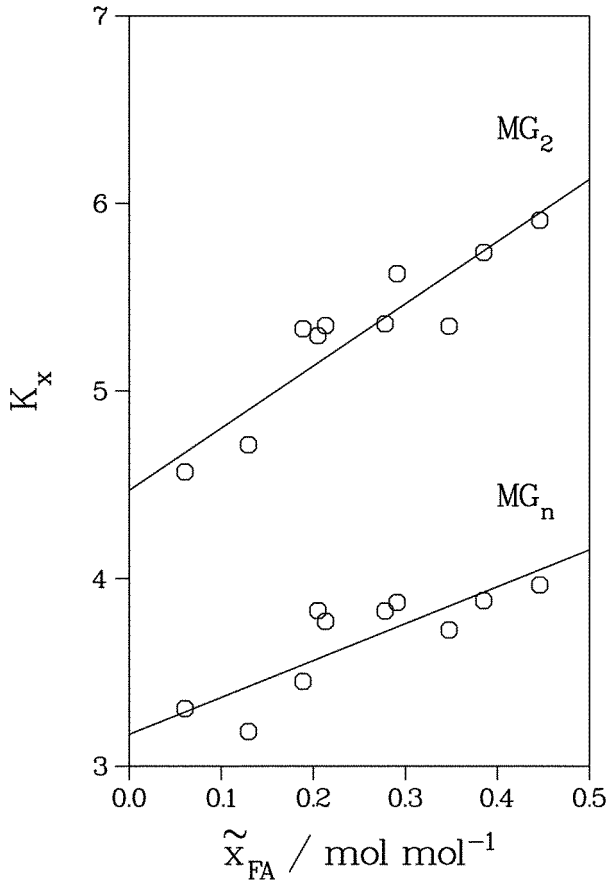

Figure 7. Equilibrium constants K_x of poly(oxymethylene) glycols formations in the formaldehyde–water system; ○, this work.

to

$$\Delta_R h^V_{MG}/(\mathrm{kJ\cdot mol^{-1}}) = \frac{43.374}{\left(1+\dfrac{37.954}{T/\mathrm{K}}\right)^2}. \qquad (10)$$

Conclusion

Aqueous solutions of formaldehyde are processed by, for example, distillation, absorption, and desorption, in many industrial applications. In order to make a basic design of such processes, a reliable model of the thermodynamic properties of formaldehyde-containing mixtures has to be available. Since formaldehyde is a very reactive component, the model has to account not only for differences in the intermolecular forces but also for chemical reactions. The reliability of such a model depends a great deal on the underlying experimental data, for example, on data for the phase equilibrium as well as on the chemical equilibrium. In the present work, the model presented by Maurer (1986) is revised and extended using not only data from the literature but also new experimental data for the vapor–liquid and the chemical equilibrium of the binary system of formaldehyde and water. The new vapor–liquid equilibrium data cover very dilute aqueous solutions (formaldehyde concentrations as low as 0.07 mass %)—for example, it is important in environmental processes to clean aqueous effluents—as well as very concentrated formaldehyde solutions (up to 71 mass %)—for example, it is important in the production of polyacetal plastics. ^{13}C-NMR spectroscopy proved to be a very efficient method for providing new and reliable chemical equilibrium data. The revised model provides a reliable description of the vapor–liquid equilibrium of the binary formaldehyde + water system from about 290 K to about 420 K, from very dilute to very concentrated concentrations, that is, up to the region where formaldehyde oligomers precipitate out of the aqueous solution. Because the model considers physical interactions and chemical-reaction equilibria, it can be extended to describe the thermodynamic properties of multicomponent formaldehyde–water mixture. Furthermore, as it correctly describes the distribution of formaldehyde to oligomers, it can also be incorporated in models to describe kinetic phenomena, such as chemical reaction and transport kinetics, which are very important in separation processes at around ambient temperature.

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Notation

A = parameter
B = parameter
C = parameter
$\Delta_R h^V_{MG}$ = reaction enthalpy for the formation of methylene glycol in the vapor phase
E_k = CH_2O–end group MG_k
Mi_k = CH_2O–middle group MG_k
Mo = CH_2O–group in methylene glycol
p = pressure
p^θ = standard pressure (101.325 kPa)
T = temperature
x = true mole fraction in liquid phase
$\tilde{x}$ = overall mole fraction in liquid phase
y = true mole fraction in vapor phase
$\tilde{y}$ = overall mole fraction in vapor phase
δ = chemical shift
γ = activity coefficient normalized according to Raoult's law

Subscripts and superscripts

i = component i
S = saturation
∞ = infinite dilution

Literature Cited

Albert, M., "Thermodynamische Eigenschaften formaldehydhaltiger Mischungen," PhD Diss., Univ. Kaiserslautern, Kaiserslautern, Germany (1999).

Albert, M., I. Hahnenstein, H. Hasse, and G. Maurer, "Vapor–Liquid Equilibrium of Formaldehyde Mixtures: New Data and Model Revision," *AIChE J.*, **42**, 1741 (1996).

Balashov, A. L., S. M. Danov, A. Yu. Golovkin, V. L. Krasnov, A. N. Ponomarev, and I. A. Borisova, "Equilibrium Mixture of Polyoxymethylene Glycols in Concentrated Aqueous Formaldehyde Solutions," *Russ. J. Appl. Chem.*, **69**, 190 (1996).

Credali, L., L. Mortillaro, G. Galiazzo, M. Russo, and C. De Checci,

''Pressione di Vapore sul Sistema H_2O-CH_2O Liquido e Solido,'' *Chim. Ind.*, **47**, 732 (1965).
Fredenslund, Aa., J. Gmehling, and P. Rasmussen, *Vapor − Liquid Equilibria Using UNIFAC, a Group Contribution Method*, Elsevier, Amsterdam (1977).
Günther, H., *NMR Spectroscopy, Basic Principles, Concepts, and Application in Chemistry*, 2nd ed., Wiley, New York (1994).
Hahnenstein, I., M. Albert, H. Hasse, C. G. Kreiter, and G. Maurer, ''NMR-Spectroscopic and Densimetric Study of Reaction Kinetics of Formaldehyde Polymer Formation in Water, Deuterium Oxide, and Methanol,'' *Ind. Eng. Chem. Res.*, **34**, 440 (1995).
Hahnenstein, I., H. Hasse, C. Kreiter, and G. Maurer, ''^{1}H- and ^{13}C NMR-Spectrocopic Study of Chemical Equilibria in Solutions of Formaldehyde in Water, Deuterium Oxide and Methanol,'' *Ind. Eng. Chem. Res.*, **34**, 1022 (1994a).
Hahnenstein, I., H. Hasse, Y.-Q. Liu, and G. Maurer, ''Thermodynamic Properties of Formaldehyde Containing Mixtures for Separation Process Design,'' *AIChE Symp. Ser.*, **90**(298), 141 (1994b).
Hasse, H., ''Dampf-Flüssigkeits-Gleichgewichte, Enthalpien und Reaktionskinetik in formaldehydhaltigen Mischungen,'' PhD Diss., Univ. Kaiserslautern, Kaiserslautern, Germany (1990).
Kogan, L. V., Yu. M. Blazhin, S. K. Ogorodikov, and V. V. Kafarov, ''Liquid-Vapor-Equilibrium in the System Formaldehyde-Water (Thermodynamic Verification with Chemical Interactions in the Liquid Phase Taken into Account),'' *Zhur. Prikl. Khim.*, **50**, 2682 (1977).
Kogan, L. V., ''State of the Vapor Phase above Solutions of Formaldehyde in Water and Methanol,'' *Zh. Prikl. Khim.*, **52**, 2722 (1979).
Le Botlan, D. J., B. G. Mechin, and G. J. Martin, ''Proton and Carbon-13 Nuclear Magnetic Resonance Spectrometry of Formaldehyde in Water,'' *Anal. Chem.*, **55**, 587 (1983).
Liu, Y.-Q., H. Hasse, and G. Maurer, ''Enthalpy Change on Vaporization of Aqueous and Methanolic Formaldehyde Solutions,'' *AIChE J.*, **38**, 1693 (1992).
Maurer, G., ''Vapor-Liquid Equilibrium of Formaldehyde- and Water-Containing Multicomponent Mixtures,'' *AIChE J.*, **32**, 932 (1986).
Siling, M. I., and B. Ya. Akselrod, ''Spectrophotometric Determination of Equilibrium Constants of the Hydration and Protonation of Formaldehyde,'' *Russ. J. Phys. Chem.*, **42**, 1479 (1968).
Walker, J. F., *Formaldehyde*, 3rd ed., Reinhold, New York (1964).

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