New Experimental Results for the Vapor−Liquid Equilibrium of the Binary System (Trioxane + Water) and the Ternary System (Formaldehyde + Trioxane + Water)

Michael Albert,[†,‡] **Hans Hasse,**[†,§] **Christian Kuhnert,**[†,||] **and Gerd Maurer***[,†]

Lehrstuhl für Technische Thermodynamik, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

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New experimental results for the vapor−liquid equilibrium of the binary system (trioxane + water) at 393 K and 413 K and the ternary system (formaldehyde + trioxane + water) at 413 K and around 450 kPa are reported and compared with predictions/correlations using a physicochemical model combining the UNIFAC equation for the Gibbs excess energy with chemical reaction equilibria. Revised parameters of the model for these systems are reported.

Introduction

Trioxane is a cyclic trimer of formaldehyde. It is an important intermediate in the production of polyacetal plastics from formaldehyde. In the production of such polymers, formaldehyde is usually converted to trioxane in acidic aqueous solutions. Trioxane is recovered by distillation. The basic design of such processes requires, for example, a model for the vapor−liquid equilibrium of the chemical reactive system formaldehyde + water + trioxane. Continuing previous work on the phase equilibrium of aqueous and methanolic solutions of formaldehyde, this work presents new experimental data for the vapor−liquid phase equilibrium of the binary system (trioxane + water) and the ternary system (formaldehyde + trioxane + water). Because reliable results for the binary vapor−liquid equilibrium of (trioxane + water) were available only for temperatures between 338 K and 383 K (Serebrennaya and Byk,[1] Kováč and Žiak,[2] Hasse et al.,[3] Brandani et al.[4]) and recent process developments tend to perform separations at higher temperatures, the vapor−liquid equilibrium of the binary system (trioxane + water) was investigated at higher temperatures (i.e., at 393 K and 413 K). The experimental results are compared to predictions from a correlation of the vapor−liquid equilibrium that was parametrized at lower temperatures.

Experimental results for the vapor−liquid equilibrium of multicomponent aqueous solutions of formaldehyde are also desired as modern separation processes for such mixtures run at elevated pressures (e.g., at around 0.5 MPa, corresponding to temperatures around 410 K). Because reliable experimental data for the vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water) is available only for temperatures up to about 370 K and at rather low trioxane concentrations (up to about 8 mol %) (Maurer;[5] Hasse et al.[3]), that vapor−liquid equilibrium was investigated at 413 K (and around 0.4 MPa) at rather low formaldehyde concentrations (between about 2 and 10 mol %) but up to high concentrations of trioxane (between about 1 and 90 mol %). The experimental data were at first compared to predictions from a previously published phase-equilibrium model (Hasse et al.[3]). However, because the predictions were not sufficiently accurate, the model was revised by adjusting some model parameters.

Experimental Section

Apparatus. A special thin-film evaporator apparatus was used for the vapor−liquid equilibrium experiments. That apparatus was used and described before (Hasse;[6] Albert et al.[7]); therefore, only an outline is given here. The thin-film evaporator consists of a rotating coil (made up of glass-fiber reinforced Teflon) inside a stainless steel tube. That coil spreads a constant, thermostated liquid feed on the inner surface of the tube. The tube is heated from the outside by a liquid that is thermostated to a few kelvins above the temperature of the liquid feed. The heating results in a partial evaporation of the liquid feed at nearly constant pressure. That pressure is supplied by a back-pressure regulator. For measurements above ambient pressure, the evaporator chamber is pressurized from a storage tank (filled with nitrogen gas). For measurements at lower pressures, the storage tank is replaced by a buffer container that is connected to a vacuum pump and a nitrogen flask. After passing the heated section of the tube, the coexisting and equilibrated phases are separated. The liquid phase is subcooled, and the gaseous phase is completely condensed. Both are separately collected in vials.

The temperature was measured (with an accuracy of ±0.1 K) with a calibrated platinum resistance thermometer. The pressure was measured with a calibrated pressure transducer with a maximum uncertainty of ±0.5 kPa. Samples of the coexisting phases of the binary system (trioxane + water) were analyzed by gas chromatography by applying the internal standard procedure. Commercially available equipment from Hewlett-Packard (GC: HP 5890 A; capillary column: Ultra 2, $l = 50$ m, $d = 0.2$ mm, $s = 0.33$ μm; thermal conductivity cell; integrator: HP 3390A; autosampler model HP-7673) was used. The internal standard was dioxane. The concentration of trioxane in the

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* Corresponding author. E-mail: gmaurer@rhrk.uni-kl.de. Phone: +49 631 205 2410. Fax: +49 631 205 3835.

[†] University of Kaiserslautern.

[‡] Current address: Degussa AG, 67547 Worms, Germany.

[§] Current address: Institut für Techn. Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart, 70550 Stuttgart, Germany.

[||] Current address: Robert Bosch GmbH, 70469 Stuttgart, Germany.

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liquid (vapor) phase was between 0.4 (2.0) and 76 (48) mol %. The maximum relative uncertainty of the experimental results for the concentration of trioxane is ±4%.

Samples of the coexisting phases of the ternary system (formaldehyde + trioxane + water) were analyzed

- for formaldehyde by wet chemistry by applying the sodium sulfite method (Walker[8]) and

- for trioxane by gas chromatography using the equipment described before, but with a packed column (Porapak T, l = 6 ft, $^{80}/_{100}$ mesh from Alltech, Unterhaching, Germany).

The stoichiometric concentration of formaldehyde in the liquid (vapor) phase was between 2.2 (5.8) and 13.7 (19.5) mol %. The stoichiometric concentration is defined here as the overall concentration (i.e., neglecting all chemical reactions). The maximum relative uncertainty of the experimental results for the concentration of formaldehyde is ±2%. The concentration of trioxane in the liquid (vapor) phase was between 1.1 (3.8) and 90 (57) mol %. The maximum relative uncertainty of the experimental results for the concentration of trioxane is ±4%.

The concentration of water was not determined independently but calculated from the mass balance. However, in a few cases (especially for the samples with lower water concentration), the results (and its uncertainty) were checked and confirmed by Karl Fischer titration.

Materials and Sample Preparation. The liquid feed mixtures of trioxane and water were prepared by gravimetric analysis. The liquid feed mixtures of (formaldehyde + trioxane + water) were also gravimetrically prepared from trioxane and aqueous solutions of formaldehyde. Aqueous solutions of formaldehyde were prepared by boiling paraformaldehyde in deionized water at a high pH. The turbid solution was filtered, and the stoichiometric formaldehyde concentration was determined by wet chemistry (cf. above). The aqueous solutions of formaldehyde were additionally analyzed by gas chromatography, but no significant impurities were detected. Trioxane (min 99% specified by GC) and paraformaldehyde (puriss.) were from Merck GmbH, Darmstadt, Germany, and used as supplied.

Experimental Results

The new experimental results for the vapor−liquid equilibrium of the binary system (trioxane + water) are given in Table 1. As expected, this binary system reveals azeotropic behavior. The new experimental results for the vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water) are given in Table 2 and shown in Figures 4 and 5. In the investigated range of states (i.e., at low formaldehyde concentrations), formaldehyde is always the most volatile component, followed either by water (at high concentrations of water) or by trioxane (at high concentrations of trioxane), as was expected from the azeotropic behavior of the binary system (trioxane + water).

Correlation and Comparison with Literature Data

Table 1. Experimental and Correlation Results for the Vapor−Liquid Equilibrium of the Binary System (Trioxane (1) + Water (2))

T/K	$\tilde{x}_1$	$\tilde{y}_{1,\mathrm{exptl}}$	$\tilde{y}_{1,\mathrm{calcd}}$	$\Delta\tilde{y}_1$/%	p_{exptl}/kPa	p_{calcd}/kPa	Δp/%
393.2	0.0345	0.1396	0.1464	4.9	226.8	226.2	−0.3
393.2	0.0396	0.1511	0.1595	5.6	226.9	228.6	0.8
393.1	0.0953	0.2353	0.2441	3.7	246.2	245.2	−0.4
393.0	0.4983	0.3482	0.3366	−3.3	252.3	250.8	−0.6
412.2	0.0040	0.0199	0.0214	7.6	363.9	357.9	−1.7
412.5	0.0071	0.0308	0.0367	19	371.2	365.5	−1.5
413.2	0.0110	0.0435	0.0538	24	383.4	378.6	−1.3
413.2	0.0132		0.0629		390.0	381.8	−2.1
413.1	0.0192	0.0732	0.0854	17	394.6	387.5	−1.8
413.2	0.0211	0.0827	0.0920	11	399.6	391.1	−2.1
413.1	0.0319	0.1134	0.1244	9.7	409.0	400.9	−2.0
413.2	0.0546	0.1624	0.1732	6.6	432.1	419.1	−3.0
413.1	0.1007	0.2098	0.2285	8.9	441.9	436.3	−1.3
413.2	0.1009	0.1933	0.2286	18	441.1	447.9	−0.7
413.0	0.1212	0.2303	0.2432	5.6	445.9	439.9	−1.3
413.2	0.3210	0.3516	0.2954	−16		450.4	
413.2	0.4342	0.3629	0.3137	−14		447.6	
413.0	0.4360	0.3266	0.3141	−3.8	450.1	445.6	−1.0
413.1	0.5267	0.3437	0.3348	−2.6		439.4	
413.1	0.7619	0.4757	0.4512	−5.2	385.2	385.4	0.1
$\bar{\Delta}$				5.2			−1.2
σ				12			1.5

Maurer[5] described the vapor−liquid equilibrium of the binary system (trioxane + water) by combining the UNIFAC equation for the Gibbs excess energy (Fredenslund et al.[9]) for the liquid mixture with the assumption that the vapor phase behaves like an ideal gas. Because water and trioxane were treated as pure components, the UNIFAC model reduces to the UNIQUAC model by Abrams and Prausnitz.[10] Hasse et al.[3] revised the UNIFAC parameters on the basis of more experimental data that covered the temperature range from about 338 K to 383 K. As has been shown by Albert,[11] that model also gives reliable predictions for the vapor−liquid equilibrium at 393 K and 413 K. In the meantime, the experimental data basis was extended by Brandani et al.,[4] the set of UNIQUAC parameters was revised by fitting to the experimental results by Hasse et al.[3] (at 93 kPa) and Brandani et al.[4] (at temperatures between 338 K and 368 K) and those of the present work (at 393 K and 413 K). The vapor pressure of each pure component was approximated by the Antoine equation. The Antoine parameters are given in Table 3 together with the pure-component UNIFAC parameters. The UNIFAC interaction parameters are given in Table 4. For fixed temperature and liquid-phase composition, the new correlation represents the new vapor−liquid equilibrium data of the binary system trioxane + water (given in Table 1) with standard deviations of 12% (for the mostly small vapor-phase mole fraction of trioxane) and 1.5% (for the total pressure). The largest deviations are observed for the vapor-phase mole fraction of trioxane above water-rich solutions at 413 K, where the correlation overshoots the experimental data resulting in relative deviations of about 20%. The new correlation gives very good agreement with the literature data. The data of Serebrennaya and Byk[1] (and of Kováč and Žiak[2]) are represented (when the liquid composition and the pressure − 101 kPa − are set) with standard deviations of 9% (and 6.4%) in the vapor-phase mole fraction of trioxane and maximum deviations in the temperature of 0.9 K (and 0.4 K). The experimental results reported by Hasse et al.[3] (at 93 kPa) are described (when the liquid-phase composition and the pressure are set) with a standard deviation of 3.2% in the trioxane concentration in the vapor phase and a maximum deviation of 0.4 K in the temperature. The experimental results for the total pressure given by Brandani et al.[4] for 338 K, 348 K, 358 K, and 368 K are described (when the liquid-phase composition and the temperature are set) with standard deviations of 1.4%, 0.9%, 1.3%, and 1.7%, respectively. As a typical example, Figure 2 shows a comparison with the experimental data of Brandani et al.[4] at 358 K.

The correlation for the vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water) is an extension of the phase equilibrium model for the binary system (formaldehyde + water). That model has been

Table 2. Experimental and Correlation Resultsfor the Vapor−Liquid Equilibrium of the Ternary System (Formaldehyde (1) + Trioxane (2) + Water (3))

T/K	$\tilde{x}_1$	$\tilde{x}_2$	$\tilde{y}_{1,\mathrm{exptl}}$	$\tilde{y}_{1,\mathrm{calcd}}$	$\Delta\tilde{y}_1$/%	$\tilde{y}_{2,\mathrm{exptl}}$	$\tilde{y}_{2,\mathrm{calcd}}$	$\Delta\tilde{y}_2$/%	p_{exptl}/kPa	p_{calcd}/kPa	Δp/%
413.1	0.1091	0.0110	0.1865	0.1967	5.4	0.0378	0.0413	9.2	427.9	425.2	−0.6
413.2	0.1056	0.0478	0.1711	0.1736	1.5	0.1364	0.1311	−3.8	462.9	455.7	−1.6
413.2	0.1368	0.0587	0.1994	0.1996	0.1	0.1466	0.1421	−3.1	478.8	466.9	−2.5
413.1	0.0400	0.0925	0.0789	0.0821	4.0	0.1953	0.2041	4.5	461.0	453.6	−1.6
413.1	0.0609	0.0933	0.1070	0.1119	4.6	0.2013	0.1994	−0.9	470.1	461.9	−1.7
413.1	0.0854	0.0953	0.1385	0.1403	1.3	0.1939	0.1952	0.7	478.9	469.5	−2.0
413.1	0.0468	0.2084	0.0856	0.0906	5.8	0.2509	0.2603	3.7	478.8	472.3	−1.4
413.1	0.0241	0.3206	0.0563	0.0607	7.9	0.2812	0.2878	2.4	471.9	465.6	−1.4
413.2	0.0357	0.4691	0.0943	0.0889	−5.7	0.3196	0.3078	−3.7	474.0	468.8	−1.1
413.2	0.0308	0.5280	0.0901	0.0865	−4.0	0.3030	0.3217	6.2	465.0	463.4	−0.4
413.2	0.0306	0.6541	0.0936	0.1034	10	0.3766	0.3619	−3.9	462.2	446.8	−3.3
413.3	0.0224	0.8975	0.1673	0.1693	1.2	0.5711	0.5692	−0.3	364.5	345.4	−5.2
	$\bar{\Delta}$			2.7			0.9			−1.9	
	σ			5.4			4.5			2.4	

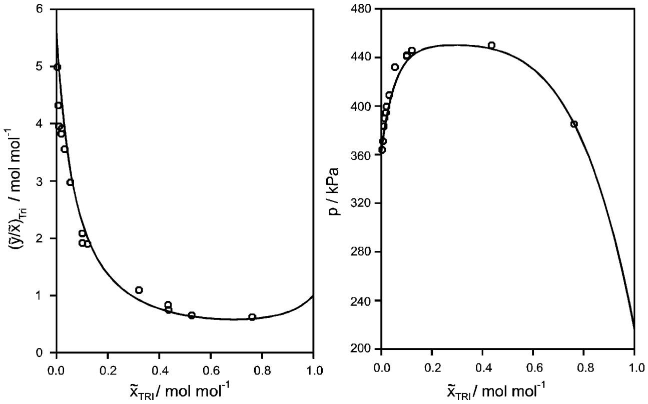

Figure 1. Trioxane + water: new results for the vapor−liquid equilibrium of the binary system at 413 K: ○, exptl results; −, correlation.

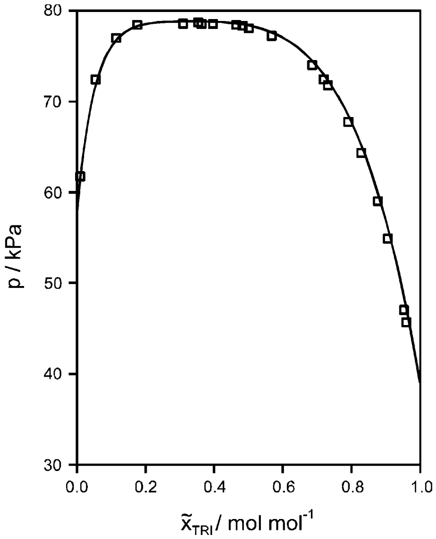

Figure 2. Vapor pressure p above aqueous solutions of (trioxane + water) at 358 K: comparison between the experimental results of Brandani et al.[4] and the correlation of the present work.

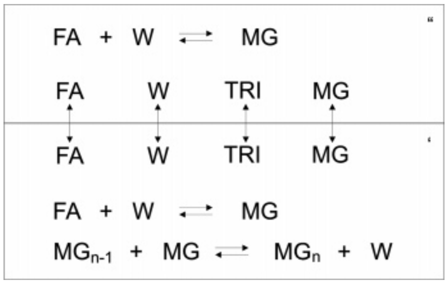

Figure 3. Scheme for modeling the vapor−liquid equilibrium in ternary mixtures of (formaldehyde + trioxane + water).

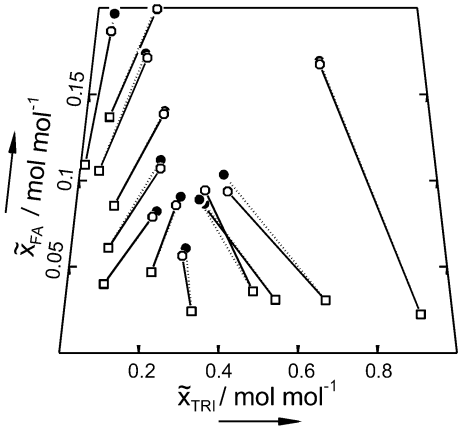

Figure 4. Vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water) at 413 K: comparison between experimental and calculated results for the vapor-phase composition (calculation for given temperature and stoichiometric liquid-phase composition). □, Liquid phase, experimental results; ○ and ●, vapor phase, experimental and calculated results, respectively.

described in detail in previous publications (cf. Maurer[5] and Albert et al.[13,14]). Therefore, only an outline of that model is repeated here.

Figure 3 shows a scheme of the vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water). Formaldehyde is a very reactive compound. Upon dissolution in water, nearly all formaldehyde is converted to a wide variety of poly(oxymethylene glycols) in equilibrium reactions. 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):

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \tag{I}$$

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

In the physicochemical model developed previously (Maurer[5]), it is assumed that the liquid phase is a mixture of water, (very little molecular) formaldehyde, methylene glycol, and a large variety of poly(oxymethylene) glycols. The chemical reaction equilibria are combined with physical interactions resulting in a powerful tool for describing vapor−liquid equilibria and caloric properties of formaldehyde-containing mixtures. This model has been continuously updated, and its application range has been extended over the last two decades as new reliable data became

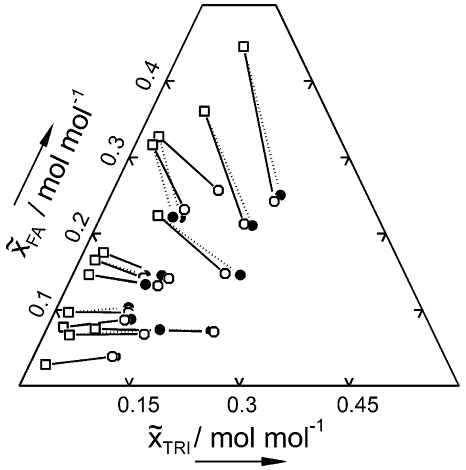

Figure 5. Vapor−liquid equilibrium of the ternary system (formaldehyde + trioxane + water) at about 368 K: comparison between experimental (Maurer[5]) and calculated results for the vapor-phase composition (calculation for given temperature and stoichiometric liquid-phase composition). □, Liquid phase, experimental results; ○ and ●, vapor phase, experimental and calculated results, respectively.

Table 3. Vapor Pressure of Pure Components ($\ln p_i^s = A_i + B_i/T/K + C_i$) and UNIFAC Size ($r_i$) and Surface ($q_i$) Parameters of Pure Components/Groups

component/group i	A_i	B_i	C_i	r_i	q_i
formaldehyde[a]	14.4625	−2204.13	−30.15	0.9183	0.78
water[a]	16.2886	−3816.44	−46.13	0.920	1.40
trioxane[b]	14.3796	−3099.47	−68.92	2.754	3.30
methylene glycol[c]	17.4364	−4762.07	−51.21	2.6744	2.94
OH				1.00	1.20
CH_2				0.6744	0.54

[a] Reid et al.[17] [b] Albert.[11] [c] Kuhnert.[12]

Table 4. Group Assignment and UNIFAC Interaction Parameters

group number	1	2	3	4	5	6
component/group	CH_2O	H_2O	$C_3H_6O_3$	$HO(CH_2O)H$	OH	CH_2
formaldehyde	1					
water		1				
trioxane			1			
methylene glycol				1		
poly(oxymethylene)-glycol $HO(CH_2O)_nH$ ($n > 1$)	$n - 1$				2	1

available. The chemical reaction equilibrium is expressed through chemical reaction equilibrium constants for the formation of methylene glycol from formaldehyde and water (reaction I) in the liquid phase

$$K_1 = \frac{a_{MG}}{a_{FA}a_W} = \frac{x_{MG}}{x_{FA}x_W}\frac{\gamma_{MG}}{\gamma_{FA}\gamma_W} \tag{1}$$

and for the formation of poly(oxymethylene) glycols

$$K_n = \frac{a_{MG_n}a_W}{a_{MG_{n-1}}a_{MG}} = \frac{x_{MG_n}x_W}{x_{MG_{n-1}}x_{MG}}\frac{\gamma_{MG_n}\gamma_W}{\gamma_{MG_{n-1}}\gamma_{MG}} \quad (n = 2, 3, 4, 5, ...) \tag{2}$$

Activities a_i are normalized according to Raoult's law (i.e., the reference state is the pure liquid at system temperature and pressure). However, the influence of pressure on the activity of a component in the liquid phase is neglected. Information on the chemical reaction equilibrium in aqueous solutions of formaldehyde caused by reactions (II) is available from high-resonance-frequency nuclear magnetic resonance (NMR) spectroscopy (cf. Balashov et al.,[15] Albert et al.,[14] Maiwald et al.[16]). Information on the chemical equilibrium due to reaction I in the vapor phase is also available (from volumetric investigations of the gaseous phases of formaldehyde and water).

$$K_1^{gas} = \frac{y_{MG}}{y_{FA}y_W}\frac{p(0)}{p} \tag{3}$$

That equilibrium constant K_1^{gas} is converted to the equilibrium constant in the liquid phase K_1 through

$$K_1 = K_1^{gas}\frac{p_{FA}^s}{p_{MG}^s}\frac{p_W^s}{p^{(0)}} \tag{4}$$

The corresponding equilibrium constants were taken from previous work (Albert et al.,[14] Kuhnert[12]):

$$\ln K_1^{gas} = -16.984 - 5233.2/(T/K) \tag{5}$$

$$\ln K_2 = 0.005019 + 834.5/(T/K) \tag{6}$$

$$\ln K_n = 0.01312 + 542.1/(T/K) \text{ for all } n \geq 3 \tag{7}$$

The vapor pressures of formaldehyde and methylene glycol were also taken from previous work (cf. Table 3).

As discussed in previous publications (Kováč et al.[3], Maurer,[5] Hasse,[7] Albert et al.,[13] Albert et al.[14]), the vapor phase is treated as a mixture of ideal gases (water, formaldehyde, and methylene glycol). The Gibbs excess energy of the liquid mixture is described by the UNIFAC group contribution method. The group assignment, the size, and surface parameters of the groups and the group interaction parameters are given in Tables 3 and 4.

The 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 is available. Deviations between measured and calculated values are typically below 5% for the partition coefficient of formaldehyde and 2% for the pressure. In the extension of that model to the ternary system (formaldehyde + trioxane + water), trioxane is considered to be an inert substance. The vapor phase is still treated as an ideal gas mixture, and the Gibbs excess energy of the liquid phase is also described by the UNIFAC model. For applying the model, the UNIFAC parameters for interactions between trioxane on one side and either methylene glycol or (the groups of) poly(oxymethylene) glycols on the other side are also required. In previous work, these additional UNIFAC parameters were estimated by the parameters for interactions between

- formaldehyde (instead of trioxane) on one side and either the OH− or the CH_2− group on the other side and
- water (instead of trioxane) on one side and methylene glycol on the other side, whereas
- no difference was made for interactions between formaldehyde on one side and trioxane on the other side (i.e., the UNIFAC parameters for interactions between formaldehyde and trioxane were set to zero).

In the present modification, the first two assumptions were adopted, but nonzero parameters for interactions between formaldehyde and trioxane were introduced. These two interaction parameters were adjusted to give a good representation of the new experimental results for the vapor−liquid equilibrium for the ternary system (formaldehyde + trioxane + water) at temperatures between 343

Table 5. UNIFAC Interaction Parameters $a_{i,j}$/K

group i	group j	1	2	3	4	5	6
1			867.8[a]	$a_{1,3}(T)$[b]	189.2[c]	237.7[c]	83.36[c]
2		−254.5[a]		80.63	189.5[c]	−229.1[c]	300.0[c]
3		$a_{3,1}(T)$[b]	379.4		379.4[d]	237.7[e]	83.36[f]
4		59.20[c]	−191.8[c]	80.63[d]		−229.1[c]	300.0[c]
5		28.06[c]	353.5[c]	28.06[e]	353.5[c]		156.4[c]
6		251.5[c]	1318[c]	251.5[f]	1318[c]	986.5[c]	

[a] Kuhnert.[12] [b] $a_{1,3}(T) = 554.9 - 2.476(T/\text{K})$; $a_{3,1}(T) = 16\,980.0 - 39.47(T/\text{K})$. [c] Albert et al.[13] [d] Approximated by parameters for interactions between trioxane and water. [e] Approximated by parameters for interactions between CH_2O and OH. [f] Approximated by parameters for interactions between CH_2O and CH_2.

K and 413 K. The influence of temperature on these parameters was also taken into account. The final set of UNIFAC interaction parameters is given in Table 5.

The comparison between the results of the correlation and the new experimental data is given in Table 2. For the experimentally determined temperature and liquid-phase composition, the standard deviations between the calculated and measured data for the vapor-phase concentrations of formaldehyde and trioxane amount to 5.4% and 4.5%, respectively. For the pressure, that standard deviation is 2.4%. Figure 4 shows some selected but typical comparisons (for the composition of the vapor phase).

A similar comparison for the experimental results reported by Hasse et al.[3] (for data points at around 343 K and 32 kPa) results in standard deviations of 2.5%, 5.3%, and 0.7% for the vapor-phase concentrations of formaldehyde and trioxane and the pressure, respectively. In comparison to the experimental data reported by Maurer[5] (26 data points at around 369 K and 100 kPa), the standard deviations are 4,8%, 8.3%, and 2.0% for the vapor-phase concentrations of formaldehyde and trioxane and the pressure, respectively. A typical comparison with some of the concentration data reported by Maurer[5] is shown in Figure 5. The agreement between the correlation results and the experimental data is considered to be satisfactory, in particular with respect to the experimental difficulties encountered in such investigations of formaldehyde-containing solutions.

Conclusions

The new experimental data for the vapor−liquid equilibrium of the binary system (trioxane + water) and the ternary system (formaldehyde + trioxane + water) and the correlation based on that data may be used for the design of separation equipment in the production of polyacetal plastics from formaldehyde. Extensions of the model to include other components that are important in the production process of polyacetals are in progress currently.

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Nomenclature

A_i = parameter of the vapor-pressure equation
a_i = thermodynamic activity of species i (normalized according to Raoult's law)
$a_{i,j}$ = UNIFAC parameter for interactions between groups i and j
B_i = parameter of the vapor-pressure equation
C_i = parameter of the vapor-pressure equation
K_1 = equilibrium constant for reaction I in the liquid phase
K_2 = equilibrium constant for reaction II ($n = 2$)
K_n = equilibrium constant for reaction II ($n \geq 3$)
K_1^{gas} = equilibrium constant for reaction I in the vapor phase
MG = methylene glycol
MG_n = poly(oxymethylene) glycol consisting of n formaldehyde groups
N = number of experimental points
n = number of formaldehyde groups
p = pressure
$p^{(0)}$ = 101.35 kPa standard pressure
p_i^{s} = vapor pressure of component i
r = UNIFAC size parameter
q = UNIFAC surface parameter
T = temperature
x_i = mole fraction of species i in the liquid phase
$\bar{x}_i$ = stoichiometric mole fraction of component i in the liquid phase
y_i = mole fraction of species i in the vapor phase
$\bar{y}_i$ = stoichiometric mole fraction of component i in the vapor phase

Greek Symbols

$\Delta z = 100(z_{\text{calcd}} - z_{\text{exptl}})/z_{\text{exptl}}$ = relative deviation between experimental result and a calculated number for property z
$\overline{\Delta z} = (100/N)\sum_{i=1}^{N}((z_{\text{calcd}} - z_{\text{exptl}})/z_{\text{exptl}})_i$ = average relative deviation between experimental results and calculation results for property z
γ_i = activity coefficient of species i (normalized according to Raoult's law)
$\sigma = 100(1/(N-1)\sum_{i=1}^{N}((z_{\text{calcd}} - z_{\text{exptl}})/z_{\text{exptl}})_i^2)^{1/2}$ = standard deviation of property z

Subscripts

calcd = calculated result
exptl = experimental result
FA = formaldehyde
MG = methylene glycol
MG_n = poly(oxymethylene) glycol consisting of n formaldehyde groups
TRI = trioxane
W = water

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