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Vapor−Liquid and Liquid−Liquid Equilibria in Binary and Ternary Mixtures of Water, Methanol, and Methylal

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Methylal is a byproduct in industrial processes, for example, in the production of polyacetal plastics. In such processes aqueous solutions of methylal and methanol have to be treated by distillation. This contribution reports experimental results for the phase equilibrium in such mixtures: vapor−liquid equilibrium of the binary systems (water + methylal) at $284 \le T/\mathrm{K} \le 388$ and (methanol + methylal) at $303 \le T/\mathrm{K} \le 348$, and of the ternary system (water + methanol + methylal) at $303 \le T/\mathrm{K} \le 363$, as well as liquid−liquid equilibrium of (water + methylal) and (water + methanol + methylal) at $273 \le T/\mathrm{K} \le 313$. Furthermore, new experimental results are reported for the vapor pressure of methylal at $318 \le T/\mathrm{K} \le 357$. The new experimental phase equilibrium data are correlated using the UNIQUAC model to describe the Gibbs excess energy of the liquid mixtures.

Introduction

Methylal is a byproduct in the production of trioxane, which again is an important intermediate in the production of polyacetal plastics from formaldehyde. In such processes aqueous and methanolic solutions of methylal have to be treated, for example, by distillation and/or extraction. Thermodynamic properties of aqueous solutions of methylal and methanol are required for designing such processes. As literature data on phase equilibrium of binary mixtures containing methylal is scarce (cf. Table 1) and no data are available for the ternary system (methylal + water + methanol), the present contribution aims to extend the experimental database on the vapor−liquid and liquid−liquid equilibria in such systems at temperatures from 273 K to 388 K. Furthermore, the phase equilibrium data are correlated by applying the UNIQUAC model for the Gibbs excess energy of the liquid mixtures.

Experimental Section

The vapor−liquid equilibrium measurements were carried out with three experimental methods: For the experiments at subambient pressures, headspace chromatography and a recirculating still technique were used, whereas measurements at elevated pressures were performed with a special thin-film evaporator. Additionally, the liquid−liquid equilibrium of (water + methylal) and (water + methanol + methylal) was investigated by analyzing the coexisting, equilibrated liquid phases. Furthermore, the vapor pressure of pure methylal was measured at temperatures between the normal boiling temperature (315 K) and 357 K.

Table 1. Literature Data for the Vapor−Liquid Phase Equilibrium of the Binary Systems (Methylal + Water) and (Methanol + Methylal)

type	author	year	*p*, *T*	*N*
	Water + Methylal			
T, *p*, *x*, *y*	Smirnov and Volkova[1]	1977	101 kPa	4
T, *p*, *x*	Bourgom[2]	1924	101 kPa	7
T, *p*, *x*	Holderbaum[3]	1995	313 K	28
azeotrope	Lesteva et al.[4]	1967	101 kPa	1
azeotrope	Lecat[5]	1949	101 kPa	1
azeotrope	Ghysels[6]	1924	101 kPa	1
azeotrope	Holderbaum[3]	1995	313−363 K	3
$\gamma^{\infty}_{\mathrm{MAL}}$	Shaffer and Daubert[7]	1969	297 K	1
T, x', x''	Bourgom[2]	1924	316−433 K	15
	Methanol + Methylal			
T, *p*, *x*, *y*	Azaryan and Svinarenko[8]	1970	101 kPa	20
T, *p*, *x*	Gilmutdinova et al.[9]	1976	101 kPa	11
azeotrope	Lesteva et al.[4]	1967	101 kPa	1
azeotrope	Lecat[5]	1949	101 kPa	1
azeotrope	Ghysels[6]	1924	101 kPa	1

Materials. Methylal ($H_3COCH_2OCH_3$, CAS. No. 109-87-5, $M = 76.1$), also known as dimethoxymethane or formaldehyde dimethyl acetal, is one of several reaction products of formaldehyde with methanol. In methanol solutions, formaldehyde is predominantly bound as hemiformal ($HOCH_2OCH_3$) and polyoxymethylene hemiformals ($HO(CH_2O)_nCH_3$, $n > 1$). The reactions leading to these products are

$$CH_2O + CH_3OH \rightleftharpoons HOCH_2OCH_3 \tag{I}$$

$$HO(CH_2O)_{n-1}CH_3 + HOCH_2OCH_3 \rightleftharpoons HO(CH_2O)_nCH_3 + CH_3OH \qquad n > 1 \tag{II}$$

Favored by low pH and high temperatures, in (methanol + formaldehyde) solutions, also the formation of acetals (polyoxymethylene dimethyl ethers, $H_3CO(CH_2O)_nCH_3$, $n \ge 1$) is observed

$$HO(CH_2O)_nCH_3 + CH_3OH \rightleftharpoons H_3CO(CH_2O)_nCH_3 + H_2O \tag{III}$$

Methylal is the first member of the series of acetals of

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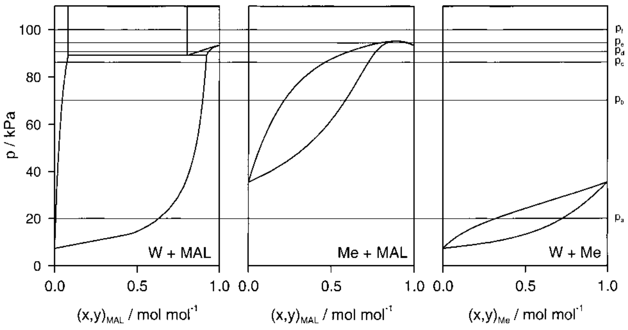

Figure 1. Phase behavior of the binary systems—from left to right—(water + methylal), (methanol + methylal), and (water + methanol) at 313 K (p^{S}_{W} = 7 kPa, p^{S}_{Me} = 35 kPa, p^{S}_{MAL} = 93 kPa, $p^{L_1L_2V}_{W+MAL}$ = 89 kPa, $p^{(az)}_{Me+MAL}$ = 95 kPa).

formaldehyde with methanol. Generally methylal is the predominant acetal in (methanol + formaldehyde) solutions, but in some cases also dimethoxy dimethyl ether ($H_3CO(CH_2O)_2CH_3$) is found, whereas the concentrations of high-molecular polyoxymethylene dimethyl ethers are very small.

Methylal and methanol were purchased in the highest available quality: methylal, Fluka No. 47875, ≥99%; methanol, Merck No. 106012, ≥99.5%. All specified concentrations were given as area percentages from a GC analysis. These materials were used as supplied. Water was deionized and twice distilled.

Discussion of Phase Behavior. For a better understanding, the phase behavior of the systems studied is discussed before the experimental results are presented. That discussion is restricted to a single temperature, as the essential features of the phase behavior do not change over the entire temperature range. The phase diagrams were constructed using the UNIQUAC model with parameters determined from experimental data (for details, see the section Correlation and Discussion).

(1) Binary Systems. Figure 1 shows schematic pressure—concentration diagrams for the binary systems (water + methylal), (methanol + methylal), and (water + methanol) at 313 K. For each system the same pressure scale is used. Additionally, some pressures are marked, for a later discussion of the phase behavior of the ternary system (water + methanol + methylal).

(2) Water + Methylal. The binary phase behavior of the binary system (water + methylal) is characterized by large differences in the vapor pressure of the pure substances and a three-phase vapor—liquid—liquid line at a pressure close to but below the vapor pressure of methylal (at 313 K: $p^{L_1L_2V}_{W+MAL}$ = 89 kPa and p^{s}_{MAL} = 93 kPa). Some authors[3-6] report a homogeneous azeotropic point in the methylal rich vapor—liquid region. However, the evaluation of experimental data in this region is very difficult due to the low water concentration in both phases. Therefore, the literature data do not allow for a reliable statement about the presence of an azeotropic point.

(3) Methanol + Methylal and Water + Methanol. The phase behavior of these systems is simpler than that of the system (water + methylal), as no liquid—liquid miscibility gap is observed. The binary system (methanol + methylal) has an azeotropic point in the methylal-rich corner (at 313 K: $p^{(az)}_{Me+MAL}$ = 95 kPa), but the pressure is less than 2 kPa above the saturation pressure of pure methylal. As is well-known, there is no azeotropic point in the binary system (water + methanol).

(4) Ternary System. The phase behavior of the ternary system (water + methanol + methylal) is shown quantitatively in Figure 2 in triangular Gibbs phase diagrams for 313 K and six pressures between 20 and 100 kPa. These pressures are also marked in Figure 1. At 20 kPa a vapor—liquid equilibrium region stretches out from the binary system (water + methanol) to the binary system (water + methylal). When the pressure rises above the saturation pressure of methanol (p^{S}_{Me}(313 K) = 35 kPa) the vapor—liquid equilibrium region stretches out from the binary system (water + methylal) to the binary system (methanol + methylal). With further increasing pressure there appears a three-phase vapor—liquid—liquid region at a critical end point where two liquid phases coexist with a vapor phase (at 313 K: $p^{(L_1=L_2)V}_{W+Me+MAL}$ = 86 kPa). The three-phase region exists only in a very small pressure range and disappears at the three-phase pressure of the binary system (water + methylal), for example, at 313 K: $p^{L_1L_2V}_{W+MAL}$ = 89 kPa. There are two two-phase regions at somewhat higher pressures (e.g. at 91 kPa): a vapor—liquid equilibrium region stretching out between the binary systems (water + methylal) and (methanol + methylal) and a liquid—liquid equilibrium region which starts from the binary system (water + methylal). When the pressure rises above the saturation pressure of methylal (p^{S}_{MAL}(313 K) = 93 kPa), the vapor—liquid region is restricted to very small water concentrations and starts/ends in the binary system (methanol + methylal) and disappears at the azeotropic point of that binary system (at 313 K: $p^{(az)}_{Me+MAL}$ = 95 kPa). At higher pressures, for example, at 100 kPa, there is only a liquid—liquid equilibrium region.

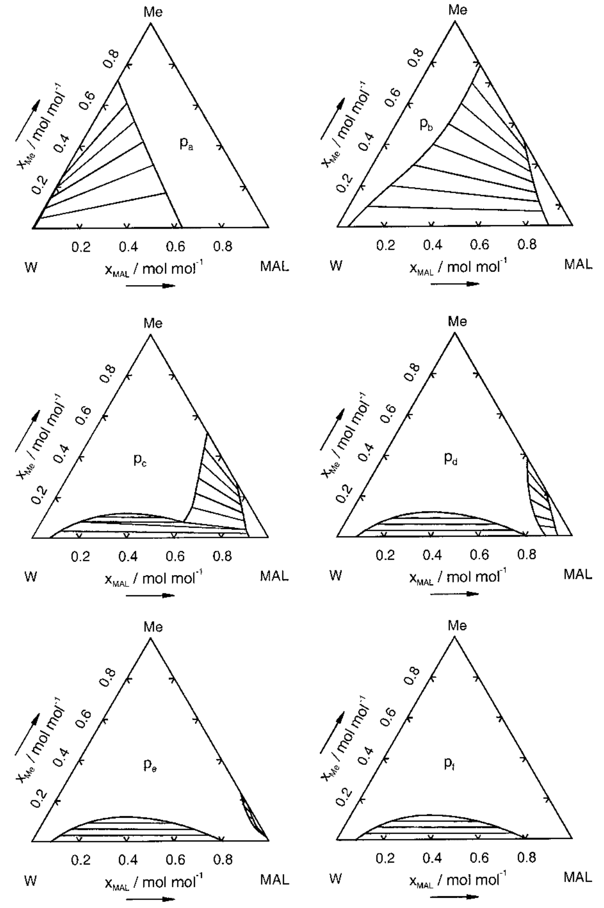

Figure 2. Phase behavior of the ternary system (water + methanol + methylal) at 313 K and pressures between 20 and 100 kPa (p_i/kPa = (20, 70, 87, 91, 94, and 100) for (i = a, b, c, d, e, and f, respectively)—cf. also Figure 1; $p^{(L_1=L_2)V}_{W+ME+MAL}$ = 86 kPa).

Vapor Pressure of Pure Methylal. The vapor pressure of methylal was measured using a stainless steel cylinder (≈40 cm^3) with valves for filling and purging and connections for temperature and pressure sensors. The temperature was measured with a calibrated platinum resistance thermometer. The pressure was measured with calibrated pressure transducer gauges from WIKA, Klingenberg, Germany. The uncertainty of the experimental results is ±0.1 K for the temperature and ±0.3% for the pressure. The cylinder was thermostated in a liquid bath. The experiments were restricted to temperatures above the normal boiling point of methylal ($T^S_{MAL} = 315$ K). After the cylinder was placed in the bath, first, the purge valve was left open to allow all low-boiling impurities and air to evaporate. Then the valve was closed and the sample was allowed to equilibrate before temperature and pressure were measured.

Vapor−Liquid Equilibrium Measurements. Three techniques were used for the measurement of the vapor−liquid equilibrium: a conventional recirculating still technique, headspace gas chromatography, and a thin film evaporating technique. As details of the equipment have been reported before,[10−12] only some essentials are repeated here. Most of the measurements of vapor−liquid equilibrium at subambient pressures were carried out with the recirculating still. In those experiments, the pressure and temperature were measured with a mercury gauge (Dosch, Berlin, Germany; uncertainty ±0.5 kPa) and a calibrated platinum resistance thermometer (uncertainty ±0.1 K). Samples of the liquid phase and the (condensed) vapor phase were analyzed by gas chromatography (cf. the section Gas Chromatographic Analysis). However, in experiments with the system (water + methylal) the condensation of the gas phase can lead to a liquid−liquid phase split. Therefore, it was not possible to determine the vapor-phase composition particularly at low methylal concentrations and no experimental results for that composition are reported.

To overcome that situation, complementary studies were made for the binary system (water + methylal) by headspace gas chromatography. The apparatus used is our own design based on the description by Hussam and Carr.[13] The sample vials (≈12 cm^3) were filled with a liquid mixture of known composition and placed into a thermostat. For headspace analysis the vapor phase of a vial was connected to a sample loop of a gas chromatograph (Hewlett-Packard, type HP 5390, thermal-conductivity detector; packed column, Porapak P) via a multiposition valve. The temperature of the vials was measured with a calibrated platinum resistance thermometer placed in the thermostating liquid medium with an uncertainty of ±0.1 K. The composition of the liquid phase in the vials was known from preparing the samples by weighing the components using an analytical balance (resolution: ±0.0001 g). Taking into account additional small uncertainties which can result from the partial evaporation of the sample in a vial, the overall relative uncertainty of the composition of the liquid is estimated to be below ±2%. The vapor-phase composition was determined from the ratio of the peak areas using calibration curves. For calibration, the vials were charged with the pure liquids and the vapor pressure was varied by changing the temperature from 273 to 313 K (water) and from 258 to 313 K (methylal). The peak areas could be reproduced within ±1% in the calibration procedure as well as in the experiments. The overall relative error in the experimental results for the partial pressure is below 5% (except for concentrations below about 2 mol %, where the absolute accuracy of about ±0.05 mol % is the limiting factor).

Table 2. New Experimental Data for the Vapor Pressure of Methylal

T/K	p^S_{MAL}/kPa	T/K	p^S_{MAL}/kPa
317.80	109.1	337.34	205.0
322.57	128.2	342.21	236.9
327.45	150.5	347.12	272.9
327.92	152.9	352.02	312.4
332.54	177.0	356.80	354.3
332.80	178.4		

At higher pressures the vapor−liquid equilibrium experiments were done with a special thin-film evaporator. In that apparatus, a rotating coil spreads a liquid feed on the inner surface of a tube. Heating the tube with a thermostated liquid results in a partial evaporation of the feed at a constant pressure. The coexisting and equilibrated phases are separated, cooled/condensed, and collected in vials. Temperature and pressure were measured with a calibrated platinum resistance thermometer and with calibrated pressure transducer gauges from WIKA, Klingenberg, Germany. The uncertainty of the experimental results is ±0.1 K for the temperature and ±0.2% for the pressure. The composition of the phases was determined by gas chromatography (cf. the section Gas Chromatographic Analysis).

Liquid−Liquid Equilibrium. The liquid−liquid equilibrium was determined by taking samples from the equilibrated coexisting liquid phases in a thermostated flask. The temperature was measured in the flasks with calibrated platinum resistance thermometers with an uncertainty of ±0.1 K. All experiments were carried out at ambient pressure in the presence of air. The equilibration of the phases was achieved by stirring with magnetic bars for several hours. The equilibrated phases were separated under gravity. Samples of each phase were removed by syringes through separate connections. The samples were analyzed by gas chromatography (cf. the section Gas Chromatographic Analysis).

Gas Chromatographic Analysis. The samples were analyzed by gas chromatography applying the “internal standard” method. The gas chromatograph was from Hewlett-Packard (model HP 5890 A). It was equipped with an autoinjector, a column from Hewlett-Packard (Ultra 2, fused silica capillary column), and a thermal-conductivity detector. Dioxane (from Fluka, No. 42502, ≥99.5%) was used as internal standard in most cases. Generally, for calibration as well as for analysis, each sample was analyzed at least five times. Relative deviations between the single results were below 2% in most cases. It is estimated that the relative error in the composition of an analyzed phase does not exceed 4%. In a few cases the analysis of an aqueous sample was checked by Karl Fischer titration. These additional measurements confirmed the estimated uncertainty of the gas chromatographic analysis.

Experimental Results

Vapor Pressure of Methylal. The experimental results for the vapor pressure of methylal are given in Table 2. The new vapor pressure data smoothly extend literature data[14−16] to higher temperatures. The Antoine equation was used to correlate all experimental results (i.e. from about 273 to 357 K). Coefficients of the Antoine equation are given in Table 3. Deviations between correlated and measured data are generally below 0.1 K for temperature and 1% for pressure, respectively.

Table 3. Vapor Pressure of Pure Components[a]

component	A	B	C	T_{min}/K	T_{max}/K
water	16.2886	−3816.44	−46.13	284	441
methanol	16.5725	−3626.55	−34.29	257	364
methylal	14.2473	−2640.84	−41.22	273	357

[a] $\ln(p^s/\text{kPa}) = A + B/[(T/\text{K}) + C]$.

Table 4. Water + Methylal: Isobaric Vapor−Liquid Equilibrium (from Experiments with a Recirculating Still)

p/kPa = 66.7			p/kPa = 93		
x_{MAL}/mol %	y_{MAL}/mol %	T/K	x_{MAL}/mol %	y_{MAL}/mol %	T/K
0.01		361.7	0.01		370.6
0.02		361.5	0.02		370.5
0.03		361.1	0.03		370.2
0.04		360.5	0.04		369.5
0.05		360.5	0.05		369.5
0.07		359.8	0.11		367.3
0.12		357.6	0.15		366.1
0.20		356.1	0.23		363.0
0.23		353.1	0.26		361.9
0.40		348.3	0.35		359.4
0.45		347.1	0.45		356.7
0.46		347.0	0.69		351.1
0.51		347.8	0.81		349.1
0.62		344.6	0.96		346.0
0.87		338.9	1.00		345.6
0.92		339.4	1.36		340.9
0.97		336.4	1.61		338.0
1.48		332.0	1.73		337.0
2.52		322.2	86.30	92.59	313.4
2.96		319.8	89.74	93.03	313.1
85.88	93.57	304.4	88.52	93.04	313.2
88.42	93.84	304.3	94.85	93.65	312.9
89.76	94.07	304.2	91.52	94.07	313.1
91.20	94.62	304.1	93.84	95.05	313.0
93.43	95.22	304.0	96.04	96.39	312.9
93.83	95.59	304.0	97.74	97.76	312.9
95.88	96.62	303.9	98.80	97.86	312.8
97.66	97.86	303.9			

Table 5. Water + Methylal: Isothermal Vapor−Liquid Equilibrium (from Experiments with a Thin-Film Evaporator)

T/K	x_{MAL}/mol %	y_{MAL}/mol %	p/kPa
323.1	2.58	84.23	70.3
	2.60	84.48	71.3
	2.85	83.18	77.1
	3.55	82.16	87.0
333.1	0.28	19.77	27.2
	0.36	23.98	28.3
	0.38	34.75	32.2
	1.10	63.40	55.6
	1.25	68.13	67.5
	1.86	75.68	83.3
388.1	0.11	3.71	177.6
	0.40	11.56	202.2
	0.91	40.19	305.3
	2.24	61.83	492.9
	2.41	61.84	491.7

Vapor−Liquid and Liquid−Liquid Equilibrium. The experimental results for the vapor−liquid equilibrium of the binary system (water + methylal) are given in Table 4 (recirculating still technique), Table 5 (thin film evaporation technique), and Table 6 (headspace gas chromatography). Tables 7 and 8 give the experimental results for the vapor−liquid equilibrium of the binary system (methanol + methylal), and Tables 9 and 10 those of the ternary system (water + methanol + methylal). The experimental results for the liquid−liquid equilibrium in the system (water + methanol + methylal) are presented in Table 11.

Table 6. Water + Methylal: Isothermal Vapor−Liquid Equilibrium (from Headspace Gas Chromatography)

	water-rich side		methylal-rich side	
T/K	x_{MAL}/mol %	γ_{MAL}	x_W/mol %	γ_W
283.5	0.48	11.8	1.46	22.0
	1.03	11.3	1.87	17.8
	1.52	11.5	3.09	17.4
	2.04	11.1	3.88	15.7
	2.94	10.6		
293.4	0.48	13.3	1.46	17.8
	1.03	12.7	1.87	18.0
	1.52	12.4	3.09	15.9
	2.04	11.6	3.88	14.9
	2.94	11.2		
303.3	0.48	14.7	1.46	18.3
	1.03	13.6	1.87	16.7
	1.52	12.8	3.09	14.9
	2.04	13.4	3.88	14.0
	2.94	12.3		
313.0	0.48	15.7	0.44	21.8
	1.03	14.4	1.06	18.6
	1.52	14.6	1.46	16.8
	2.04	14.0	1.87	14.7
	2.94	12.6	3.09	13.7
			3.88	13.0

Table 7. Methanol + Methylal: Isobaric Vapor−Liquid Equilibrium (from Experiments with a Recirculating Still)

p/kPa = 66.7			p/kPa = 93.3		
x_{MAL}/mol %	y_{MAL}/mol %	T/K	x_{MAL}/mol %	y_{MAL}/mol %	T/K
0.08	0.51	327.4	0.13	0.79	334.8
0.24	1.55	327.3	0.27	1.62	334.5
0.70	4.47	326.5	0.54	3.22	334.2
1.30	8.08	325.8	0.72	4.16	334.0
2.03	12.13	324.8	0.93	5.28	333.8
2.66	15.32	324.1	2.58	13.43	331.8
3.67	18.90	323.3	3.01	15.30	331.5
5.18	26.45	321.7	4.77	22.17	329.8
7.44	33.56	319.4	6.72	28.51	328.1
9.70	39.83	317.5	8.77	34.46	326.5
12.36	45.35	315.8	9.14	34.80	326.8
15.36	50.34	314.3	11.76	41.21	324.5
19.47	56.12	312.4	15.01	43.93	323.8
22.95	59.64	311.0	15.13	47.50	322.6
25.35	61.52	310.2	18.95	53.22	320.8
30.60	65.34	308.9	19.64	51.11	321.7
34.10	67.18	308.1	24.18	56.83	319.8
38.01	69.06	307.5	27.80	60.21	318.6
40.57	70.37	307.1	31.04	64.48	317.4
48.33	73.25	306.1	41.09	69.05	315.9
63.22	78.39	304.8	45.90	71.22	315.2
72.27	81.41	304.2	58.78	75.47	313.9
81.19	85.17	303.8	67.11	78.69	313.3
85.73	87.43	303.6	78.95	83.70	312.6
87.71	88.70	303.5	84.09	86.03	312.5
89.60	89.83	303.5	88.95	88.89	312.3
93.60	93.07	303.5	91.23	90.70	312.1
97.73	97.27	303.7	98.26	97.79	312.7
			99.16	98.86	312.8

Correlation and Discussion

Correlation. For the correlation of the new binary vapor−liquid equilibrium data, the vapor phase was treated as an ideal gas and the influence of pressure on the liquid-phase properties was neglected:

$$p_i^s x_i \gamma_i = p y_i \tag{1}$$

The pure component vapor pressures were described by the Antoine equation. For water and methanol the Antoine parameters were taken from Reid et al.[17] They are given in Table 3. Activity coefficients γ_i were described by the

Table 8. Methanol + Methylal: Vapor−Liquid Equilibrium at 348 K (from Experiments with a Thin-Film Evaporator)

x_{MAL}/mol %	y_{MAL}/mol %	p/kPa	x_{MAL}/mol %	y_{MAL}/mol %	p/kPa
1.15	5.10	158.6	64.04	71.36	289.3
2.51	10.17	165.4	77.43	78.06	297.1
11.73	33.16	209.2	82.91	82.02	294.7
16.65	40.70	225.1	89.63	87.78	294.1
40.13	59.06	262.6			

Table 9. Water + Methanol + Methylal: Isobaric Vapor−Liquid Equilibrium (from Experiments with a Recirculating Still)

p/kPa	x_{Me}/mol %	x_{MAL}/mol %	y_{Me}/mol %	y_{MAL}/mol %	T/K
66.7	25.33	1.49	44.13	29.31	333.0
	5.30	1.40	12.15	60.20	333.1
	30.62	13.47	17.35	74.83	312.8
	49.46	16.40	28.17	66.03	313.2
	17.19	78.46	12.39	85.79	303.1
	11.09	84.62	9.04	88.68	303.1
93.3	23.28	1.33	44.80	23.55	343.1
	5.08	1.27	12.44	49.26	343.1
	30.04	11.25	20.45	69.79	323.1
	50.47	15.17	31.60	61.27	323.1
	18.16	76.59	13.73	83.96	313.1
	11.67	82.90	9.91	87.17	312.9

Table 10. Water + Methanol + Methylal: Vapor−Liquid Equilibrium from 343 to 363 K (from Experiments with a Thin-Film Evaporator)

T/K	x_{Me}/mol %	x_{MAL}/mol %	y_{Me}/mol %	y_{MAL}/mol %	p/kPa
343.1	57.26	5.00	59.02	27.06	134.8
	59.13	7.36	55.45	30.46	151.0
	53.32	21.11	36.08	56.33	200.9
	23.28	18.55	14.62	63.58	209.8
348.1	18.15	24.46	11.83	75.50	258.9
	19.27	25.06	12.75	74.21	259.2
	35.57	56.87	26.59	69.32	
	17.80	71.77	15.36	78.40	
353.1	11.52	6.14	13.10	68.24	239.6
	0.90	4.97	1.00	80.21	279.8
363.1	13.5	5.60	17.13	60.19	295.5

Table 11. Water + Methanol + Methylal: Isothermal Liquid−Liquid Equilibrium

T/K	x'_{Me}/mol %	x'_{MAL}/mol %	x''_{Me}/mol %	x''_{MAL}/mol %
273.15	0	9.97	0	89.10
	2.32	10.35	1.01	86.24
	6.31	12.00	3.61	80.71
	8.66	13.96	5.54	75.62
	11.53	18.86	8.76	63.68
	12.36	22.55	10.32	55.34
293.15	0	9.12	0	83.96
	1.69	9.82	1.00	82.36
	2.08	10.12	1.31	81.25
	2.08	10.07	1.31	81.85
	6.79	13.74	5.27	69.15
	8.92	18.17	7.57	59.15
	9.79	23.60	9.35	47.69
313.15	0	8.19	0	82.09
	2.17	9.60	1.85	75.08
	3.92	11.20	3.41	70.41
	6.78	15.68	6.28	57.09
	7.92	19.79	7.69	47.45
	8.05	20.54	7.84	45.13

Table 12. UNIQUAC Size and Surface Parameters for Water, Methanol, and Methylal

component	r	q
water	0.9200	1.400
methanol	1.4311	1.432
methylal	2.9644	2.716

Table 13. UNIQUAC Interaction Parameters $a_{i,j}$/K

	j		
i	W	Me	MAL
W		289.6	$a_{W,MAL}(T)^a$
Me	−181.0		−71.21
MAL	$a_{MAL,W}(T)^b$	410.0	

[a] $a_{W,MAL}(T) = -225.5 + 0.7205(T/K)$. [b] $a_{MAL,W}(T) = 1031 - 1.749(T/K)$.

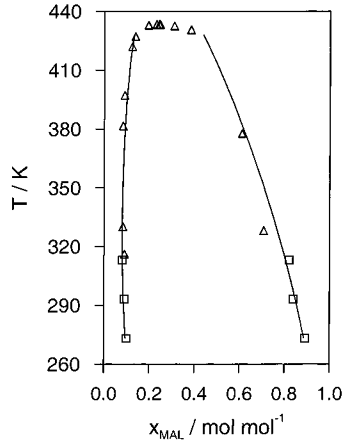

Figure 3. Water + methylal. Liquid−liquid equilibrium: △, Bourgom;[2] □, this work; —, UNIQUAC.

UNIQUAC equation.[18] Size and surface parameters for water, methanol, and methylal are given in Table 12.

Water + Methylal. Due to the liquid−liquid miscibility gap, experimental vapor−liquid equilibrium data are only available for low liquid-phase mole fractions of water as well as of methylal. Fitting both UNIQUAC parameters for interactions between water and methylal ($a_{W,MAL}$ and $a_{MAL,W}$) to that data resulted in a poor representation of the liquid−liquid equilibrium data as well as of the three-phase equilibrium. Therefore, the binary interaction parameters were simultaneously fitted to the new liquid−liquid equilibrium data as well as to the results given by Bourgom.[2] However, for a reasonable description of the liquid−liquid equilibrium, the influence of temperature on both interaction parameters had to be taken into account. The parameters are given in Table 13. The relative deviation in the concentration of methylal in the water-rich liquid and of water in the methylal-rich liquid is for most temperatures below 5%. The temperature at the critical point of the liquid−liquid equilibrium is overestimated; however, that temperature (≈445 K) is far beyond the temperature range of the present investigation. A comparison between calculated and measured liquid−liquid-phase equilibrium data is shown in Figure 3. A set of interaction parameters fitted to liquid−liquid-phase equilibrium data alone also provides a reasonable description of the vapor−liquid equilibrium data. There are large deviations between calculated and measured vapor-phase concentrations only at low methylal concentrations. However, at these low methylal concentrations a very small change in the methylal concentration of the liquid results in a large change of the methylal concentration in the vapor phase (cf. Figure 1). These rather large deviations between calculation and measurement for small methylal concentrations were accepted, as at methylal concentrations above 1 mol % the relative deviation between correlation and experiment is typically below ±3% for the methylal concentration in the vapor phase and ±3% for the pressure. The correlation also gives reasonable agreement with most

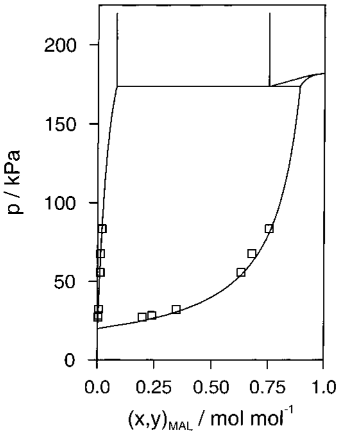

Figure 4. Water + methylal. Vapor−liquid equilibrium at 333 K: □, this work; —, UNIQUAC.

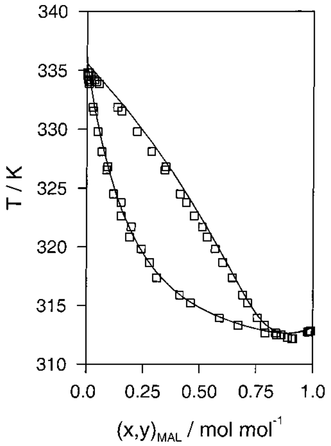

Figure 5. Methanol + methylal. Vapor−liquid equilibrium at 93 kPa: □, this work; —, UNIQUAC.

literature data. A typical example is shown in Figure 4 for 333 K.

Methanol + Methylal. The literature contains very little information on the vapor−liquid equilibrium of this system (cf. Table 1). Only Azaryan and Svinarenko[8] reported p, T, x, y data. However, those data are inconsistent. The experimental results reported by Gilmutdinova et al.[9] seem also of limited quality. Therefore, the UNIQUAC parameters $a_{\mathrm{ME,MAL}}$ and $a_{\mathrm{MAL,ME}}$ were fitted exclusively to the new experimental results for the vapor−liquid equilibrium of that binary system. The interaction parameters are given in Table 13. When temperature and liquid-phase composition are set and pressure and vapor-phase composition are calculated, the calculated numbers deviate from the experimental data by about ±2% (pressure) and ±3% (concentration of the predominant component in the vapor phase). A typical example for a comparison between experimental data (for 93 kPa) and the results from a flash calculation (i.e. temperature and pressure were set) is shown in Figure 5.

Water + Methanol + Methylal. The phase behavior of the ternary system was predicted using the UNIQUAC interaction parameters determined for the binary systems (water + methylal) and (methanol + methylal) together with parameters for (water + methanol) from Maurer[19] (cf. Table 13). The vapor−liquid equilibrium calculations were performed with preset temperature and liquid-phase composition, resulting in the pressure and the composition of the vapor phase. Typical relative deviations between predicted and measured concentrations in the vapor phase are below ±1% for methanol and ±4% for methylal. The calculated pressure agrees typically with the experimental result within ±2%. An example for such a comparison is shown in Figure 6 for the vapor−liquid equilibrium at 93 kPa. The influence of methanol on the liquid−liquid equilibrium of the system (water + methylal) is also predicted reliably. Relative deviations for the concentrations in both phases are typically below ±10% for methanol and ±8% for methylal. A typical comparison is shown in Figure 7, where the predictions for the miscibility gap at 313 K are compared to the experimental data. However, larger and systematic deviations are observed for the concentration of metyhlal in the methylal-rich liquid, particularly at lower temperatures. Those deviations are largest at the lowest temperature (i.e. 273 K) and decrease with rising temperature.

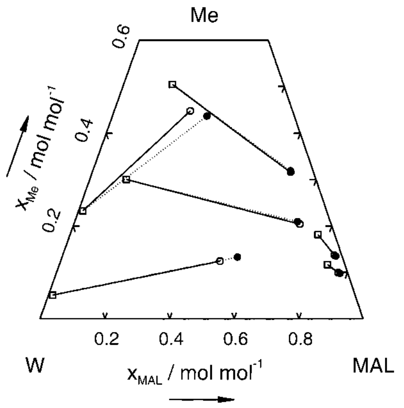

Figure 6. Water + methanol + methylal. Concentrations in vapor−liquid equilibrium at 93 kPa (temperatures between 313 and 343 K): □, liquid (this work); ○, vapor (this work); ●, prediction vapor (UNIQUAC, preset temperature and liquid-phase composition).

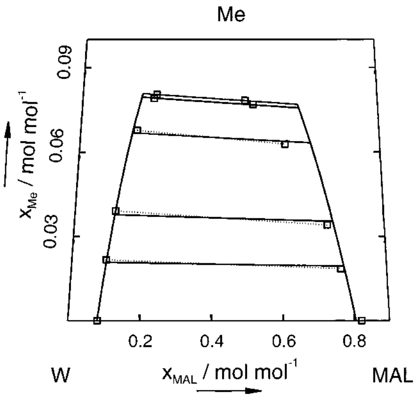

Figure 7. Water + methanol + methylal. Liquid−liquid equilibrium at 313 K: □···□, this work; —, prediction using UNIQUAC.

Conclusions

Methylal, an acetal of formaldehyde and methanol, is often present in aqueous and methanolic solutions of formaldehyde. For the design of separation equipment, the phase equilibrium of such systems, particularly the vapor−liquid equilibrium, has to be known at temperatures between about 300 and 400 K. The present work reports more than 150 experimental data points for the vapor−liquid equilibrium of the binary systems (water + methylal) and (methanol + methylal) and the ternary system (water + methanol + methylal) at temperatures between 284 and 388 K. As water and methylal are only partially miscible, the liquid−liquid equilibrium of the binary system (water

+ methylal) and the ternary system (water + methanol + methylal) was also investigated by taking 19 data points at temperatures between 273 and 313 K. Furthermore, as there are only a few literature sources, the vapor pressure of methylal was measured at temperatures between 318 and 357 K.

The phase equilibrium data for the binary mixtures were correlated assuming that the vapor behaves like an ideal gas and the activity coefficients in the liquid phase can be expressed by the UNIQUAC model. In ongoing work the results are incorporated in a model for the phase equilibrium in multicomponent mixtures containing also formaldehyde.

List of Symbols

$a_{i,j}$ = UNIQUAC interaction parameter for interactions between components i and j
A, B, C = parameters
M = molecular mass
Me+MAL = binary system (methanol + methylal)
N = number of experimental points
n = number of CH_2O groups in polyoxymethylene hemiformals and acetals
p = pressure
q = UNIQUAC surface parameter
r = UNIQUAC size parameter
T = temperature
W+MAL = binary system (water + methylal)
W+Me = binary system (water + methanol)
W+Me+MAL = ternary system (water + methanol + methylal)
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Symbols

γ_i = activity coefficient of component i normalized according to Raoults's law
γ^{∞} = activity coefficient at infinite dilution

Subscripts

i = component
MAL = methylal
Me = methanol
Me+MAL = binary system (methanol + methylal)
min = minimum
max = maximum
W = water
W+MAL = binary system (water + methylal)
W+Me = binary system (water + methanol)
W+Me+MAL = ternary system (water + methanol + methylal)

Superscripts

(az) = azeotropic point
$(L_1{=}L_2)V$ = critical end point line for three-phase equilibrium between two liquid phases L_1 and L_2 and a vapor phase V
L_1L_2V = three-phase equilibrium between liquid phases L_1 and L_2 and vapor phase V
S = saturation
$'$ = water-rich liquid phase
$''$ = methylal-rich liquid phase

Literature Cited

(1) Smirnov, V. S.; Volkova, M. I. Liquid−Vapor Equilibrium in the Systems Methylal−Trimethylcarbinol, Methylal−4,4-Dimethyl-1,3-Dioxane, and Methylal−Water. *Zh. Prikl. Khim.* **1977**, *50* (9), 2104−2105.
(2) Bourgom, A. Contribution à l'étude du méthylal comme solvant. *Bull. Soc. Chim. Bel.* **1924**, *33*, 101−115.
(3) Holderbaum, T. Personal communication of unpublished data from DDB (Dortmunder Datenbank), 1995.
(4) Lesteva, T. M.; Kachalova, R. V.; Morozova, A. I.; Ogorodnikov, S. K.; Trenke, K. M. Study of Azeotropy in Binary and Ternary Systems. *Zh. Prikl. Khim.* **1967**, *40* (8), 1808−1814.
(5) Lecat, M. *Tables Azéotropiques*, 2nd ed.; Uccle: Bruxelles, Belgium, 1949.
(6) Ghysels, M. Contribution à l'étude des formals des alcools primaires. *Bull. Soc. Chim. Bel.* **1924**, *33*, 57−78.
(7) Shaffer, D. L.; Daubert, T. E. Gas−Liquid Chromatographic Determination of Solution Properties of Oxygenated Compounds in Water. *Anal. Chem.* **1969**, *41* (12), 1585−1589.
(8) Azaryan, Z.; Svinarenko, N. V. Liquid−vapor equilibrium in the methylal−methanol system. *Fiz. Chim. Met. Anal.* **1970**, *1*, 155−159.
(9) Gilmutdinova, V. A.; Lesteva, T. M.; Khrapkova, E. I.; Chernaya, V. I. Removal of oxigen-containing imputities from isoprene by rectification. *All-Union Institute of Scientific and Technical Information of the Academy of Sciences of the USSR* (*VINITI*), Moscow, USSR, 1976; Vol. 1456−76, pp 1−15.
(10) Hasse, H. Dampf-Flüssigkeits-Gleichgewichte, Enthalpien und Reaktionskinetik in formaldehydhaltigen Mischungen. Ph.D. Thesis, Universität Kaiserslautern, Germany, 1990.
(11) Asprion, N. Anwendung der Spektroskopie in thermodynamischen Untersuchungen assoziierender Lösungen. Ph.D. Thesis, Universität Kaiserslautern, Germany, 1996.
(12) Albert, M.; Hahnenstein, I.; Hasse, H.; Maurer, G. Vapor−Liquid Equilibrium of Formaldehyde Mixtures: New Data and Model Revision. *AIChE J.* **1996**, *42*, 1741−1752.
(13) Hussam, A.; Carr, P. W. Rapid and precise method for measurement of vapor/liquid equilibria by headspace gas chromatography. *Z. Anal. Chem.* **1985**, *57*, 793−801.
(14) Nicolini, E.; Laffitte, P. Tensions de vapeur de quelques liquides organiques purs. *C. R. Séances Acad. Sci. Paris* **1949**, *229*, 757−759.
(15) McEachern, D. M.; Kilpatrick, J. E. Entropy and Related Thermodynamic Properties of Dimethoxymethane. *J. Chem. Phys.* **1964**, *41* (10), 3127−3131.
(16) Brazhnikov, M. M.; Peshchenko, A. D.; Ral'ko, O. V. Heats of Vaporization of C_1−C_4 Aliphatic Aldehydes and of Dimethoxymethane. *Zh. Prikl. Khim.* **1976**, *49* (5), 1041−1044.
(17) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(18) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.
(19) Maurer, G. Vapor-Liquid Equilibrium of Formaldehyde and Water Containing Multicomponent Mixtures. *AIChE J.* **1986**, *32*, 932−948.

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