J. Chem. Eng. Data **1994**, *39*, 184–185

Isothermal Vapor–Liquid Equilibria for the Water–1,3,5-Trioxane System

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Boiling point data have been measured for the binary mixture water–trioxane at 338, 348, 358, and 368 K. The data were reduced using Barker's method by the UNIQUAC activity coefficient model. In addition, vapor–liquid equilibrium (VLE) predictions with the obtained parameters show good agreement with isobaric experimental data available in the literature.

Introduction

Trioxane (1,3,5-trioxane) is of industrial interest because it is the basic chemical for polyacetal resin production (*1*). Trioxane is one of the downstream products in aqueous mixtures of formaldehyde. To describe these complex mixtures, it is necessary to have experimental vapor–liquid equilibrium (VLE) data of all the constituent binary systems. In the literature for the binary system water–trioxane only isobaric data are reported (*1–3*) which cover the temperature range from 362 to 378 K.

Therefore, in the present work, boiling point data for the binary mixture water–trioxane were measured at 338, 348, 358, and 368 K, and interaction coefficients for the UNIQUAC equation (*4*) were computed.

Experimental Section

The measurements were carried out in an all-glass static still, 100 cm^3 capacity. The apparatus and the operating procedures have been described elsewhere (*5*). The temperature was measured with the aid of precision Taylor thermometers within ±0.05 K. The overall accuracy in the pressure measurements was 0.05 kPa. The accuracy of the composition measurements is estimated to be within ±0.0005 mole fraction.

The equilibrium liquid compositions were obtained by gas chromatography (Perkin-Elmer 8310 with an LC-100 integrator), after calibration with gravimetrically prepared standard solutions. A thermoconductivity detector was used, together with a 6-ft, 1/8-in.-o.d. stainless steel separation column, packed with Hayesep T 80–100 mesh. The injector, oven, and detector temperatures were 413, 453, and 473 K, respectively. The carrier gas was helium, with a flow rate of 25 cm^3/min. Trioxane was reagent grade supplied by Aldrich. Its claimed purity was 99+%. Bidistilled water was used.

Table 1. Experimental Total Pressures P at Four Temperatures for the System Water (1)–1,3,5-Trioxane (2) as a Function of the Liquid-Phase Mole Fraction x_1

	P/kPa			
x_1	338.15 K	348.15 K	358.15 K	368.15 K
0.0000[a]	16.60	25.03	36.78	52.81
0.0395	21.41	31.54	45.68	64.82
0.0470	22.18	32.50	47.04	66.75
0.0942	26.00	38.29	54.90	77.47
0.1226	27.88	41.00	59.02	82.95
0.1716	30.57	44.66	64.33	90.83
0.2095	32.04	46.94	67.75	95.79
0.2688	33.56	49.40	71.78	101.53
0.2813	33.93	50.13	72.43	102.75
0.3148	34.54	51.18	74.01	105.18
0.4332	35.30	53.05	77.23	110.38
0.4995	35.50	53.37	78.06	111.62
0.5175	35.53	53.66	78.33	111.79
0.5360	35.60	53.64	78.43	112.23
0.6040	35.65	53.74	78.54	112.70
0.6373	35.73	53.78	78.55	112.70
0.6470	35.74	53.69	78.70	112.82
0.6910	35.82	53.64	78.57	112.67
0.8245	35.64	53.58	78.42	112.08
0.8865	34.90	52.82	76.99	110.27
0.9456	32.72	49.25	72.42	104.19
0.9905	27.04	41.52	61.74	89.73
1.0000[a]	24.68	38.03	57.03	83.40

[a] As calculated from the literature Antoine coefficients.

Results and Discussion

Table 1 contains the experimental VLE data measured in this work. As can be seen the water–trioxane system exhibits a positive azeotrope in the whole temperature range. The experimental data were reduced using Barker's method (*6*) with the UNIQUAC activity coefficient model. The vapor pressures of pure components were calculated with the Antoine equation using the parameters reported elsewhere (*7*). Vapor-phase nonideality was taken into account using the virial equation of state with second virial coefficients predicted from the Hayden–O'Connell correlation (*8*). Molar liquid volumes were predicted using the modified Rackett equation (*9*). The average absolute deviation on pressure for all the data is 0.12 kPa, the standard deviation is 0.15 kPa, and the maximum deviation is 0.40 kPa. The parameters of the UNIQUAC equation as a function of temperature are given by the following equations:

$$a_{12}/\mathrm{K} = 222.61 - 0.7000T/\mathrm{K} \tag{1}$$

$$a_{21}/\mathrm{K} = 462.65 - 0.5004T/\mathrm{K} \tag{2}$$

The r and q UNIQUAC parameters ($r_1 = 0.92$, $q_1 = 1.40$, $r_2 = 2.76$, $q_2 = 2.34$) were taken from ref 10.

Table 2 shows the comparison between the predicted and experimental values of boiling points and vapor compositions of isobaric VLE data. The results are in very good agreement with the most recent data (*1*). Figure 1 represents the isobaric

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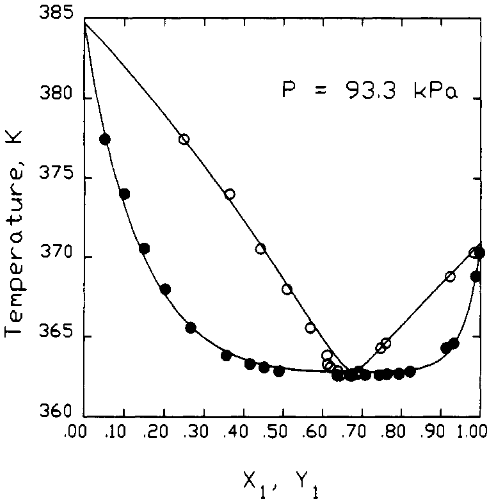

Figure 1. Isobaric phase diagram at 93.3 kPa for the water (1)–trioxane (2) system: (—) calculated; (○) experimental dew points; (●) experimental boiling points.

Table 2. Comparison between Experimental and Calculated Boiling Temperatures and Vapor-Phase Compositions at Constant Pressure *P*

	average absolute deviations		
P/kPa	ΔT/K	Δy	ref
93.3	0.34	0.0115	1
101.3	1.22	0.0216	2
101.3	1.17	0.0209	3

phase diagram of water–trioxane at 93.3 kPa. Experimental points were taken from Hasse et al. (*1*).

Glossary

a_{ij}	UNIQUAC binary parameters, K
P	total pressure, kPa
q	external surface area parameter
r	molecular size parameter
T	temperature, K
x	liquid mole fraction
y	vapor mole fraction

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Received for review December 10, 1992. Revised June 22, 1993. Accepted August 25, 1993.• The authors are indebted to the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support.

• Abstract published in *Advance ACS Abstracts,* November 15, 1993.