# Isothermal Vapor–Liquid Equilibria and Solubility in the System Methanol + 1,3,5-Trioxane

## Stefano Brandani and Vincenzo Brandani*

Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università de L'Aquila, I-67040 Monteluco di Roio, L'Aquila, Italy

Total vapor pressure data have been measured for the binary mixture methanol + 1,3,5-trioxane at 338, 343, 348, 353, 358, 363, and 368 K. The solubility of solid trioxane in methanol was determined from 293 to 328 K. The experimental data have been correlated using the UNIQUAC equation for the activity coefficient. In addition, the isobaric vapor–liquid equilibrium calculated predictions with the obtained parameters show good agreement with the experimental data available in the literature.

## Introduction

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 equilibrium data of all the constituent binary systems. In the literature for the binary system methanol + trioxane only isobaric vapor–liquid equilibrium (VLE) data are reported (*1*) which cover the temperature range from 333 to 377 K.

Therefore, in the present work, vapor pressure data for this binary mixture were measured at 338, 343, 348, 353, 358, 363, and 368 K, and the solubility of solid trioxane in methanol was investigated in the temperature range 293–328 K. Interaction coefficients for the UNIQUAC equation (*2*) were computed.

## Experimental Section

The vapor pressure measurements were carried out in an all-glass static still, 100 cm³ capacity. The apparatus and the operating procedures have been described elsewhere (*3*). 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.

To measure solubilities, mixtures of methanol and an excess of solid trioxane were equilibrated at several temperatures by stirring in a stoppered flask thermostated by circulating water. After 2 h, the stirring was stopped, and after decanting portions of solution were analyzed.

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 cm³/min. Trioxane and methanol were reagent grade supplied by Aldrich, with claimed purities of 99+% (w/w) and 99.9+% (w/w), respectively.

## Results and Discussion

Table 1 contains the experimental VLE data measured in this work. The experimental data were reduced using Barker's method (*4*) with the UNIQUAC activity coefficient model. The vapor pressures of pure components were calculated with the Antoine equation using the parameters reported elsewhere (*5*). Vapor-phase nonideality was taken into account using the virial equation of state with second virial coefficients predicted from the Hayden–O'Connell correlation (*6*). Molar liquid volumes were predicted using the modified Rackett equation (*7*).

**Table 1. Experimental Total Pressures *P* at Temperature *T* for the System Methanol (1) + 1,3,5-Trioxane (2) as a Function of the Mole Fraction $x_1$**

| $x_1$ | $P$/kPa | | | | | | |
| | 338.15 K | 343.15 K | 348.15 K | 353.15 K | 358.15 K | 363.15 K | 368.15 K |
|---|---|---|---|---|---|---|---|
| 0.0025 | 17.49 | 21.38 | 26.01 | 31.56 | 38.08 | 45.98 | 55.26 |
| 0.0220 | 22.10 | 27.13 | 33.18 | 39.85 | 47.58 | 56.04 | 65.83 |
| 0.1365 | 46.65 | 55.22 | 65.77 | 77.66 | 90.66 | 106.12 | 123.38 |
| 0.1575 | 49.96 | 59.65 | 70.66 | 83.22 | 97.46 | 114.07 | 132.88 |
| 0.1745 | 52.57 | 62.43 | 74.70 | 88.17 | 103.15 | 120.59 | 140.27 |
| 0.3320 | 71.69 | 85.79 | 101.95 | 120.42 | 141.79 | 166.11 | 193.76 |
| 0.3425 | 72.78 | 87.11 | 103.62 | 122.16 | 143.80 | 168.73 | 196.64 |
| 0.3955 | 77.10 | 92.43 | 110.22 | 130.08 | 153.48 | 180.13 | |
| 0.4680 | 82.01 | 98.51 | 117.54 | 139.38 | 164.23 | 192.73 | |
| 0.5395 | 85.82 | 103.10 | 123.44 | 146.51 | 173.25 | 203.74 | |
| 0.6440 | 90.02 | 108.60 | 130.12 | 154.52 | 183.42 | | |
| 0.7220 | 92.73 | 111.68 | 134.34 | 160.37 | 190.44 | | |
| 0.7370 | 93.39 | 112.47 | 134.95 | 161.47 | 191.58 | | |
| 0.8380 | 96.53 | 116.78 | 140.48 | 167.63 | 199.41 | | |
| 0.8730 | 97.66 | 117.98 | 142.49 | 169.84 | 201.92 | | |
| 0.9985 | 101.47 | 123.15 | 148.64 | 178.20 | | | |
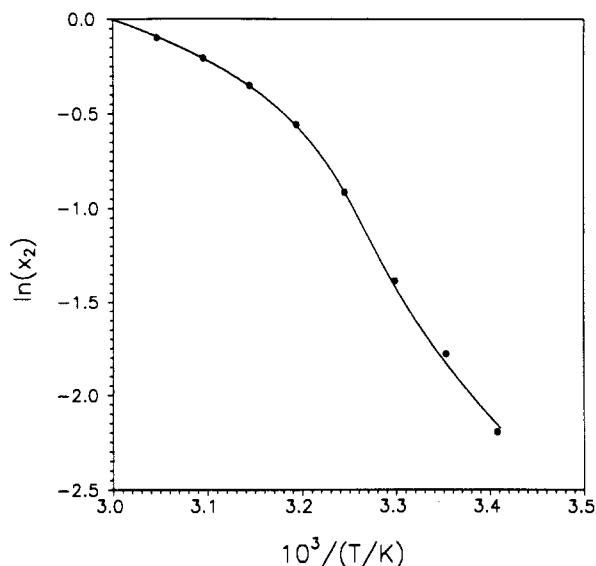
**Figure 1.** Solubility of solid 1,3,5-trioxane, mole fraction $x_2$, in liquid methanol as a function of temperature $T$: (—) calculated points; (●) experimental points.
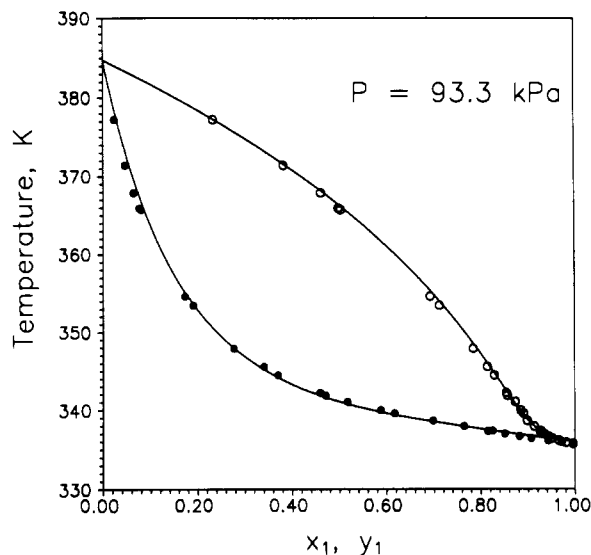


**Figure 2.** Isobaric phase diagram at 93.3 kPa for the methanol (1) + 1,3,5-trioxane (2) system: (—) calculated points; (O) experimental dew points; (●) experimental boiling points. The data are from Hasse et al. (1).

The measured solubilities are reported in Table 2. The experimental data were correlated, according to Prausnitz et al. (2), using the equation

$$\ln(\gamma_2 x_2) = -\frac{\Delta S^f}{R}\left[\frac{T_m}{T} - 1\right] \tag{1}$$

where

$$\Delta s^f = \Delta H^f/T_m \tag{2}$$

The $r$ and $q$ UNIQUAC parameters ($r_1 = 1.43$, $q_1 = 1.43$, $r_2$

**Table 2. Solubility of Solid 1,3,5-Trioxane, Mole Fraction $x_2$, in Liquid Methanol as a Function of Temperature $T$**

| $T/K$ | $x_2$ | $T/K$ | $x_2$ |
|---|---|---|---|
| 293.45 | 0.1115 | 313.10 | 0.5745 |
| 298.25 | 0.1690 | 318.05 | 0.7055 |
| 303.15 | 0.2505 | 323.05 | 0.8140 |
| 308.20 | 0.4020 | 328.25 | 0.9060 |

= 2.76, $q_2$ = 2.34) were taken from DECHEMA (8). The enthalpy of fusion, $\Delta H^f$ = 15 105 J/mol, and the melting point, $T_m$ = 333.44 K, were taken from Van Bommel et al. (9). The obtained parameters are

$$a_{12}/K = 229.00{-}0.3601(T/K) \tag{3}$$

$$a_{21}/K = 402.30{-}0.6714(T/K) \tag{4}$$

The average absolute deviation on pressure for all the data is 0.19 kPa, and the maximum deviation is 0.61 kPa. For the solubility data, the average absolute deviation on $x_2$ was 0.0044 with a maximum deviation of 0.0087. Figure 1 shows a comparison between calculated and experimental solubilities.

Figure 2 represents the isobaric phase diagram of methanol + trioxane at 93.3 kPa, calculated with the obtained parameters and the experimental points 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 |
| $R$ | ideal gas constant, J/(K mol) |
| $T$ | temperature, K |
| $T_m$ | melting point temperature, K |
| $x$ | liquid mole fraction |
| $y$ | vapor mole fraction |
| $\gamma$ | activity coefficient |
| $\Delta H^f$ | enthalpy of fusion, J/mol |
| $\Delta S^f$ | entropy of fusion, J/(K mol) |

**Literature Cited**

(1) Hasse, H.; Hahnenstein, I.; Maurer, G. *AIChE J.* **1990**, *36*, 1807.
(2) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(3) Brandani, V.; Di Giacomo, G.; Foscolo, P. U. *Ind. Eng. Chem., Process Des. Dev.* **1980**, *19*, 179.
(4) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(5) Maurer, G. *AIChE J.* **1986**, *32*, 932.
(6) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem., Process Des. Dev.* **1975**, *14*, 209.
(7) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.
(8) Gmehling, J.; Onken, U. *Vapor Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, series of volumes starting in 1977.
(9) Van Bommel, M. J.; Van Miltenburg, J. C.; Schuijff, A. *J. Chem. Thermodyn.* **1988**, *20*, 397.