44 *J. Chem. Eng. Data* **2003,** *48,* 44−47

Vapor−Liquid−Liquid Equilibrium (VLLE) and Vapor Pressure Data for the Systems 2-Methyl-1,3-dioxolane (2MD) + Water and 2,4-Dimethyl-1,3-dioxolane (24DMD) + Water

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Vapor−liquid−liquid equilibrium data for the binary systems 2-methyl-1,3-dioxolane + water and 2,4-dimethyl-1,3-dioxolane + water were collected by using a modified Othmer still vessel at 1 atm of pressure. The UNIQUAC equation of state was fitted to the experimental $T-x-x-y$ data to generate the coefficients of the binary interaction parameters for each system. Vapor pressures for pure 2,4-dimethyl-1,3-dioxolane and 2-methyl-1,3-dioxolane were also measured and used to calculate the constants in Antoine's equation and pure component parameters for each dioxolane. The enthalpy of vaporization calculated from vapor pressure data via the Clausius−Clapeyron equation was in good agreement with the literature value.

Introduction

The recovery and separation of acetals from aqueous solutions by fractional distillation is difficult because acetals form azeotropes with water. Vapor−liquid equilibrium data are thus critical for designing experiments, conducting process design, and performing economic assessment of the distillation operation. Although vapor−liquid equilibrium data for several binary systems of dioxolanes are reported in the literature,[1−4] there is no detailed information on the systems 2-methyl-1,3-dioxolane (2MD) + water and 2,4-dimethyl-1,3-dioxolane (24DMD) + water. This paper reports experimental vapor−liquid−liquid equilibrium (VLLE) data for these systems at atmospheric pressure along with vapor pressures for the dioxolanes. The VLLE data are correlated to the UNIQUAC equation of state[5] to determine the binary interaction parameters of the liquid-phase activity coefficients.

Experimental Section

Materials. Reagent grade (99.5%, Aldrich) ethylene glycol (EG), propylene glycol (PG), and acetaldehyde were used in all experiments. The pure acetals 2MD and 24DMD are not available commercially, and they were thus prepared in the laboratory by reaction of EG and PG, respectively, with acetaldehye. The procedure of Broekhuis et al.[4] was used in which EG or PG was placed with excess acetaldehyde in aqueous solution at 273 K in the presence of the acid form of a cation-exchange resin (Amberlyst 15, Aldrich). The solution was stirred for several hours, and the organic and aqueous layers were then separated in a separatory funnel. Excess acetaldehyde was removed by treatment with aqueous sodium bisulfite, and the organic layer was washed with NaOH solution to reduce its water content.[6] The acetal was then dried by addition of 3 Å molecular sieves (Aldrich) and finally distilled in an oven-dried distillation assembly. The final purity of the acetal was determined by gas chromatography to be greater than 99.5%.

Analytical Methods. Analysis of 2MD, 24DMD, and water was conducted in a Varian 3700 gas chromatograph equipped with a thermal conductivity detector. A 1.83 m × 0.00318 m o.d. (6 ft × $^1/_8$ in.) Porapak Q packed column was used at 483 K (isothermal) with a helium carrier gas flow rate of 1.6 $dm^3 \cdot h^{-1}$ (27 $cm^3 \cdot min^{-1}$). One microliter samples of liquid and condensed vapor from the Othmer still were injected; response factors for the dioxolanes and water were determined using a series of five calibration standards that spanned the range of sample compositions. Repeated injections of samples of known concentration indicated that the determined concentrations were accurate and reproducible to ±0.003 mole fraction.

Propylene glycol and ethylene glycol were analyzed using high-performance liquid chromatography (HPLC) (Thermo Separation Product Ltd.) with a refractive index detector and a Bio-Rad HPX-87C column. The separation was conducted isocratically using water at a flow rate of 0.060 $dm^3 \cdot h^{-1}$ (1.0 $mL \cdot min^{-1}$). Raw samples were diluted 2- to 3-fold with water, and an internal standard (2-propanol, 10 $kg \cdot m^{-3}$) was added to calculate species concentrations. Response factors were determined using a series of five calibration standards containing EG and PG along with the internal standard.

Collection of Equilibrium Data. The vapor−liquid−liquid equilibrium was studied at atmospheric pressure in a modified Othmer still[7] traditionally used for the collection of vapor−liquid equilibrium data. The still is equipped with a side arm for circulation of the liquid and vapor phase and sampling ports for each phase. The liquid temperature inside the still is measured with a precision of 0.1 °C by means of a calibrated glass thermometer; the vapor temperature is measured by a type K thermocouple read by a digital thermometer (Omega, Inc.). The Othmer still is insulated to maintain vapor and liquid temperatures within ±0.2 °C of each other over all conditions.

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10.1021/je025534p CCC: $25.00

Specified quantities of acetal and water were placed in the Othmer still and brought to a specified temperature for subcooled liquid−liquid equilibrium or to reflux for VLLE collection. After steady state was reached, as evidenced by continuous reflux of the condensed vapor back to the still pot and constant liquid and vapor temperatures, samples of each liquid phase and condensed vapor were taken and analyzed as described above. The VLLE diagram was generated by changing the dioxolane mole fraction in the initial still charge across the entire composition range from zero to one.

Vapor Pressure Measurement. Vapor pressure measurements were carried out for each pure acetal in a 25 mL pressure vessel (Parr Instrument Company) equipped with a pressure gauge with the range −100 kPa to +200 kPa (−30 in. Hg to +60 in. Hg). Initially, 10 mL of pure acetal was placed in the vessel, which was sealed and purged with helium. The vessel was then placed in an ice bath and allowed to equilibrate. Next, it was evacuated to remove helium and partially vaporize the acetal, with care taken not to completely boil off the acetal. The gauge pressure following evacuation, which represents the vapor pressure of the acetal at 273 K, was read and recorded. The evacuated vessel was then submerged and allowed to equilibrate in a controlled-temperature water bath with temperature measured to 0.1 °C by a type K thermocouple and readout (Omega, Inc.). The bath temperature and the corresponding final pressure gauge reading were then recorded. The bath temperature was then changed over the range 298 K to 363 K.

The acetal vapor pressure at each temperature was calculated by linearly interpolating the recorded gauge pressure between the gauge reading for absolute zero pressure and the gauge reading for atmospheric pressure (99.0 ± 0.70 kPa or 745 mmHg ± 5 mmHg). The gauge reading for absolute zero pressure was determined by evacuation of the empty vessel with a two-stage mechanical vacuum pump.

As a test of the accuracy of vapor pressure measurements, pure water was subjected to the above experimental procedure. Measured values of water vapor pressure were then compared to values from the literature.[8] For nine different temperatures ranging from 303 K to 363 K, the average difference between measured and literature values of vapor pressure was −0.9 kPa (−6.6 mmHg), and the standard deviation of the difference was 2.3 kPa (17 mmHg). Measured vapor pressures below 320 K were up to 1.3 kPa (10 mmHg) above the literature values, and values from 323 K to 363 K were on average 1.3 kPa (10 mmHg) below the literature values. The lone exception was at 363 K, the highest temperature recorded, where the measure vapor pressure of 64.1 kPa (482 mmHg) was 5.3 kPa (40 mmHg) below the accepted value of 69.4 kPa (522 mmHg). Thus, there is some systematic error in the vapor pressure measurements, and the method is less reliable at temperatures approaching the boiling point of the fluid in the flask.

The uncertainty in reading the pressure gauge was ±0.9 kPa or ±6.5 mmHg. Additional uncertainty in the measured vapor pressure arises from residual helium left in the vessel following evacuation, but on the basis of the variation in the recorded pressure at 0 °C, the partial pressure of residual helium was less than 0.7 kPa (5 mmHg) in the vessel following evacuation. The vapor pressures measured in this study thus have an uncertainty of ±2.0 kPa (±15 mmHg) at a given temperature.

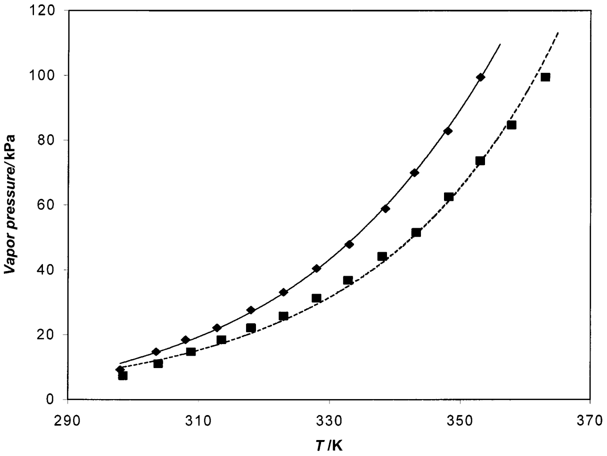

Figure 1. Vapor pressure of 2MD (◆) and 24DMD (■); lines are vapor pressure predicted using Antoine's equation with parameters in Table 1.

Table 1. Coefficients of Antoine's Equation, Enthalpies of Vaporization, and Normal Boiling Points of 2MD and 24DMD

	2MD	24DMD
Coefficients in Antoine's Equation (Eq 1, P_{sat}/kPa))		
A	16.95	14.35
B/K	4535.0	3193.2
C/K	287.2	237.5
temperature range/K	298−353	298−363
Normal Boiling Point/K		
from Antoine's equation (eq 1)	353.8	363.8
literature value[9]	355	*cis*, 363.4 *trans*, 366.2
Enthalpy of Vaporization/kJ·mol^{-1}		
from experimental data (eq 2)	35.6	34.4
literature value[9]	34.9	38.9

Results and Discussion

Vapor Pressure. The experimental vapor pressure data for 2MD and 24DMD are shown in Figure 1. Pure component vapor pressure is described by Antoine's equation.

$$\ln(P^{\mathrm{sat}}) = A - \frac{B}{(T - 273) + C} \tag{1}$$

where *T* is in kelvin. The constants *A*, *B*, and *C* (units are in the Nomenclature section) were obtained by fitting the experimental vapor pressures by nonlinear regression using Polymath software (CACHE, Inc.).

The enthalpy of vaporization for each dioxolane (ΔH_v) was calculated from the experimental data based on the Clausius−Clapeyron equation.

$$\ln(P^{\mathrm{sat}}) = -\frac{\Delta H_v}{RT} + Q \tag{2}$$

The plot of $\ln(P^{\mathrm{sat}})$ versus $1/T$ for each dioxolane is a straight line, indicating that the heats of vaporization are constant over the temperature range studied.

The constants in Antoine's equation, predicted normal boiling points, and calculated enthalpies of vaporization of 2MD and 24DMD are given in Table 1. The predicted normal boiling points and enthalpies of vaporization are reasonably close to values reported in the literature.[9]

Vapor−Liquid−Liquid Equilibrium. The experimental vapor−liquid−liquid equilibrium data at atmospheric pressure for the systems 2MD + water and 24DMD +

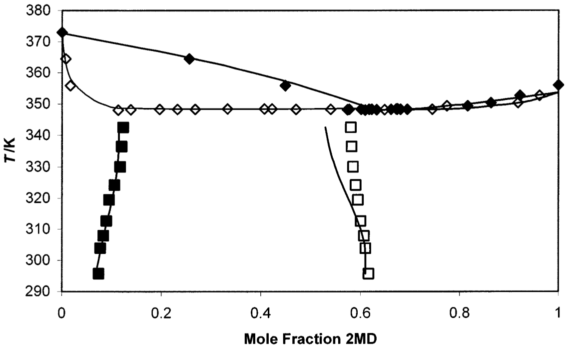

Figure 2. Experimental and predicted VLLE data for the system 2MD−water at 1 atm: (■, □) liquid−liquid; (◇) saturated liquid; (◆) saturated vapor; solid lines are predicted VLLE data using the UNIQUAC equation with binary interaction parameters from Table 5.

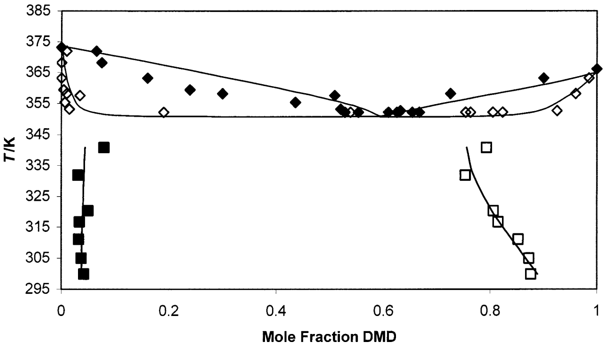

Figure 3. Experimental and predicted VLLE data for the system 24DMD−water at 1 atm: (■, □) liquid−liquid; (◇) saturated liquid; (◆) saturated vapor; solid lines are predicted VLLE data using the UNIQUAC equation with binary interaction parameters from Table 5.

Table 2. Experimental Vapor−Liquid−Liquid Equilibrium Data for the System 2MD + Water (Mole Fraction 2MD)

T/K	x_1	x_2	y	T/K	x_1	x_2	y
295.7	0.074	0.616		348.3	0.470		0.617
303.8	0.077	0.61		348.3	0.268		0.680
307.8	0.083	0.607		348.3	0.232		0.661
312.6	0.089	0.6		348.3	0.196		0.601
319.4	0.095	0.595		348.4	0.422		0.674
324.2	0.105	0.59		348.4	0.407		0.674
330.0	0.117	0.585		348.4	0.333		0.672
336.5	0.12	0.582		349.4	0.774		0.816
342.6	0.123	0.58		350.4	0.918		0.863
348.1	0.113		0.609	352.7	0.962		0.922
348.2	0.648		0.632	355.8	0.017		0.449
348.2	0.138		0.573	356.0	1.000		1.000
348.3	0.744		0.694	364.5	0.008		0.256
348.3	0.577		0.673	373.0	0.000		0.000
348.3	0.540		0.622				

Table 3. Experimental Vapor−Liquid−Liquid Equilibrium Data for the System 24DMD + Water (Mole Fraction 24DMD)

T/K	x_1	x_2	y	T/K	x_1	x_2	y
299.7	0.042	0.876		352.5	0.925		0.631
304.9	0.037	0.873		353.0	0.015		0.520
310.9	0.032	0.852		355.2	0.006		0.436
316.6	0.033	0.814		357.4	0.034		0.509
320.2	0.050	0.806		358.0	0.960		0.725
331.8	0.031	0.753		358.0	0.010		0.300
340.7	0.079	0.793		359.3	0.004		0.239
352.1	0.823		0.625	363.0	<0.003		0.160
352.1	0.805		0.667	363.0	0.985		0.900
352.1	0.763		0.653	366.0	1.000		1.000
352.1	0.754		0.528	368.0	<0.003		0.075
352.1	0.538		0.609	371.8	0.010		0.065
352.1	0.190		0.553	373.0	0.000		0.000

Table 4. Pure Component Properties[a] of 2,4-Dimethyl-1,3-dioxolane (24DMD) and 2-Methyl-1,3-dioxolane (2MD)

parameter	2MD	24DMD
SG[9]	0.981	0.930
T_c/K	553.67	558.85
P_c/bar	47.59	38.9
V_c/cm^3·gmol^{-1}	242.5	336
Z_c	0.2540	0.249
ω	0.0693	0.5128
r	3.185	4.2241
q	2.636	3.768

[a] All properties except specific gravity predicted by AspenPlus 10.2.

water are given in Figures 2 and 3, respectively, and are also tabulated in Tables 2 and 3. In addition to the presence of two liquid phases, both acetals form minimum-boiling azeotropes with water: 24DMD−water forms an azeotrope at 352.1 K and 0.54 mole fraction 24DMD, and 2MD−water forms an azeotrope at 348.4 K and 0.61 mole fraction 2MD. The 2MD−water azeotrope is reported by Horsley[10] to be at 348 K and 0.7 mole fraction 2MD, although no details are given on how it was determined. Several experimental data points with overall (combined) liquid compositions ranging from 0.2 to 0.5 for 2MD−water are omitted from Table 2. Each of these compositions gave a water-rich liquid phase of 0.14 mole fraction 2MD and a 2MD-rich liquid phase of 0.58 mole fraction 2MD in different quantities in equilibrium with the azeotropic vapor-phase composition. Several similar points were collected for 24DMD−water.

Aspen Plus 10.2 (Aspen Tech, Inc) process simulation software was used to fit the experimental VLLE data to the standard UNIQUAC equation of state, assuming the vapor is an ideal gas (a reasonable assumption at 1 atm). The UNIQUAC equation describes the liquid-phase activity coefficient γ_i for each species in the system; the full UNIQUAC expression for liquid-phase activity coefficients is described elsewhere.[5] The expression for vapor−liquid−liquid equilibrium (eq 3) is used to calculate activity

$$y_iP = \gamma_i^{I} x_i^{I} P_i^{\text{sat}} = \gamma_i^{II} x_i^{II} P_i^{\text{sat}} \tag{3}$$

coefficients from experimental data, with vapor pressures for the dioxolanes calculated from the experimentally determined Antoine's equation coefficients in Table 1. The pure component volume parameter r and surface parameter q in the UNIQUAC model were generated in AspenPlus 10.2 by group contribution methods for 2MD and 24DMD, along with pure component critical properties (T_c, P_c, V_c, and Z_c) and the acentric factor ω. These parameters are reported in Table 4. The binary interaction parameters τ_{ij} and τ_{ji} are the adjustable parameters in the UNIQUAC equation and are described as a function of temperature according to eq 4.

$$\tau_{ij} = \exp(A_{ij} + B_{ij}/T + C_{ij} \ln T + D_{ij}T) \tag{4}$$

Experimental data were entered into AspenPlus 10.2 as $T-x-y$ and $T-x-x$ sets. Data regression was then performed simultaneously with both data sets to calculate the coefficients A, B, C, and D for each binary interaction parameter τ_{ij} and τ_{ji}. The calculated binary interaction parameter coefficients are given in Table 5. The VLLE data predicted from the UNIQUAC equation using the binary interaction parameters of Table 5 are given as the solid

Table 5. UNIQUAC Binary Interaction Parameter (τ_{ij} and τ_{ji}) Coefficients for the Binary Systems 2MD + Water and 24DMD + Water

BIP coefficients (i = 2MD, 24DMD; j = H_2O)	2MD + water	24DMD + water
A_{ij}	14.07	89.06
A_{ji}	−22.83	−4.36
B_{ij}/K	6886	−11 380
B_{ji}/K	−2618	1230
C_{ij}	−11.95	−4.97
C_{ji}	8.07	−0.608
D_{ij}/K^{-1}	0.101	−0.083
D_{ji}/K^{-1}	−0.048	0.013

Table 6. Root-Mean-Square Errors of Dioxolane Mole Fractions and Temperatures Predicted by UNIQUAC Relative to Experimental Values

parameter	2MD + water	24DMD + water
x	0.013	0.013
y	0.036	0.052
T/K	0.73	2.34

lines in Figures 2 and 3. The root-mean-square errors between experimental and fitted acetal mole fractions and temperatures for 2MD−water and 24DMD−water are given in Table 6.

The VLLE data predicted by UNIQUAC describe the experimental data well for both 2MD−water and 24DMD−water. For 2MD−water, the azeotropic composition and temperature and the vapor−liquid region are described exceptionally well; the liquid−liquid phase region is described reasonably well for the water-rich phase and less so for the 2MD-rich phase. For the 24DMD−water system, liquid−liquid and vapor−liquid experimental data exhibit significant scatter because 24DMD at low concentrations in water partially hydrolyzes to propylene glycol. We collected a number of points in these regions and have included them in Figure 3 and Table 3. Despite the scatter, the predicted VLLE data reasonably represent the experimental results, including the azeotropic composition. The azeotrope temperature and 24DMD bubble point are predicted low by 1.0 to 1.5 K because the collected 24DMD vapor pressure data predict a low 24DMD boiling point.

The binary interaction parameter coefficients given in Table 5 represent a set of values that predict VLLE for the two systems. Caution must be used in applying the binary interaction parameter coefficients outside the temperature range used in experiments (298 to 373 K), as the fitted coefficients cannot be considered a unique set describing the data. We attempted to fit the VLLE data for each system with only three (A, B, C) and with only two (A, B) binary interaction parameter coefficients; with fewer parameters the quality of the fit decreased slightly. We thus present the full set of coefficients (A, B, C, D) as a representation of the best fit of the data.

Conclusions

Equilibrium data for the binary systems 24DMD−water and 2MD−water have been collected and fit to the UNIQUAC equation of state to calculate binary interaction parameters. The estimated VLLE compositions from the UNIQUAC equation agree well with the experimental data, indicating that the application of the UNIQUAC model is satisfactory and the predicted binary equilibrium data are useful for design and scale up of acetal recovery systems using distillation.

Acknowledgment

Mr. Greg Wank collected some of the experimental vapor pressure data.

Nomenclature

A, B, C = coefficients in Antoine's equation (B and C in units of kelvin)
A_{ij}, B_{ij}, C_{ij}, and D_{ij} = binary interaction parameters of components i and j in the mixture (B_{ij} in kelvin; D_{ij} in inverse kelvin)
Q = constant in the Clausius−Clapeyron equation
P^{sat} = vapor pressure (kPa)
T = temperature (K)
ΔH_v = enthalpy of vaporization (kJ·mol^{-1})
R = ideal gas constant (0.008 31 kJ·mol^{-1}·K^{-1})
x_i = mole fraction of species i in the liquid phase
y_i = mole fraction of species i in the vapor phase
γ_i = liquid-phase activity coefficient of component i
T_c = critical temperature (K)
P_c = critical pressure (bar)
V_c = critical volume (cm^3·mol^{-1})
Z_c = critical compressibility factor
ω = acentric factor
τ_{ij} = UNIQUAC binary interaction parameter
r = UNIQUAC pure component volume parameter
q = UNIQUAC pure component surface parameter

Note Added after ASAP Posting. This article was released ASAP on 11/6/2002 with errors in Table 5. The second A_{ij} entry was changed to A_{ji}. The second C_{ij} was changed to C_{ji}. The second D_{ij}/K^{-1} was changed to D_{ji}/K^{-1}. The correct version was posted on 12/10/2002.

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Received for review March 28, 2002. Accepted September 24, 2002. Support of this work by the National Corn Growers Association is gratefully acknowledged.

JE025534P