MEASUREMENT OF VAPOR-LIQUID EQUILIBRIA BY DEW-BUBBLE POINT METHOD AND BUBBLE-CONDENSATION POINT METHOD*

MASAHIRO KATO, HITOSHI KONISHI, TAKAO SATO AND
MITSUHO HIRATA

*Department of Industrial Chemistry, Tokyo Metropolitan University,
Tokyo, Japan*

Vapor-liquid equilibrium relationships of four binary systems containing dioxane were measured at atmospheric pressure without using any analytical instrument. The dew-bubble point method was used for the systems methanol-dioxane and ethanol-dioxane. For other systems, benzene-dioxane and ethyl acetates-dioxane, the bubble-condensation point method was applied in the present investigation. The experimental dew, bubble and condensation point temperatures were measured by using a flow-type apparatus. As a result, a minimum azeotrope was observed in the ethanol-dioxane system. The other three binary systems measured were nonazeotropic.

Introduction

Vapor-liquid equilibrium relationships are important properties of liquid mixtures, and isobaric data in particular are required for practical use, such as in the design of distillation equipment.

For measurement of isobaric vapor-liquid equilibria, several types of apparatus have been proposed by Othmer and some other investigators^{1,6,10}). In these conventional apparatus, it is necessary to analyze the sample. For measurement of isobaric dew points, a unique apparatus was proposed by Kojima et al.⁸). In that apparatus, it is necessary to analyze the sample and it is difficult to measure the dew point at the precise composition desired. Furthermore, the bubble points must be determined by separate measurements or by theoretical estimations. For measurement of isobaric bubble points, Cottrell²), Kojima et al.^{7,9}), and Swietoslawski¹⁴) have proposed ebulliometers. However, in the general batch type ebulliometer, it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. The dew points must be determined separately.

For measurement of isobaric dew and bubble points, two types of apparatus were previously proposed by the authors^{4,5}). Based on the dew-bubble point method, it is possible to measure vapor-liquid equilibria without analysis when using these apparatus.

Based on the bubble-condensation point method, Smith and Wojciechowski¹²) determined isobaric vapor-liquid equilibrium relationships by measuring the bubble points and the condensation points, or the bubble point temperatures of the condensed equilibrium vapors, using a differential ebulliometer. It is a simple matter to construct the dew point curve as well as the bubble point curve from the bubble and condensation point data. Using the differential ebulliometer, it is necessary to correct the difference between the liquid composition at steady state and the feed composition, and the amount of fractionation which occurs in the apparatus must be equivalent to that of one theoretical plate of a fractionating column. An apparatus previously designed by the authors⁵) could be considered to be applied to the bubble-condensation point method, based on more precise principle of determination.

In the present paper, vapor-liquid equilibrium relations have been measured by the dew-bubble point method and bubble-condensation point method for four binary systems containing dioxane, which is a useful solvent for many organic and some inorganic compounds.

Experimental Apparatus

Experimental apparatus is identical to that⁵) previously proposed for measurement of isobaric dew and bubble points and vapor-liquid equilibria. The schematic diagram of the apparatus is shown in **Fig. 1**. It is constructed entirely of borosilicate glass. Its main parts are three stills, S, four overflow tubes,

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C: Connecting tube K: Cock
F: Feeder O: Overflow-tube
H: Condenser S: Still
J: Ball-joint T: Thermometer

Fig. 1 Experimental apparatus

O, a connecting tube, C, and a feeder, F. The amount of liquid in each still is about 15 cc in volume. In each still, the boiling vapor-liquid mixture rises through a Cottrell tube and flushes to a thermometer well. The experimental temperatures were measured with mercury thermometers, calibrated to $\pm 0.1^\circ\text{C}$ in accordance with a standard platinum resistance thermometer in an Swietoslawski ebulliometer¹⁴. The standard thermometer was calibrated in the National Research Laboratory of Metrology, Japan, according to the specifications of the international practical temperature scale¹³.

Experimental Procedure

With the apparatus described above, it is possible to measure dew and bubble points and also bubble and condensation points at any desired composition without analysis.

Measurement of Dew and Bubble Points

The experimental procedure is almost identical to that described in a previous investigation⁵. First, connecting tube C is taken off. Cocks K_3 , K_4 , and K_9 are opened, and cocks K_2 , K_5 , K_6 , K_7 , and K_8 are closed. A prepared solution of the given composition is charged from feeder F continuously and the flow rate can be controlled with cock K_1 . The liquid is boiled in stills S_1 , S_2 , and S_3 . During the experi-

Fig. 2 Schematic flow diagram for measurement of bubble and condensation points

ment, the liquid from the still S_2 partially overflows through the branched tube O_2 .

As described in a previous paper⁵, the liquid composition in S_1 and S_3 , and the vapor composition in S_2 must agree with the feed composition at steady state. Therefore, the temperatures obtained in the stills, S_1 , S_2 , and S_3 , respectively, should equal the bubble point, dew point, and also bubble point of the feed composition at steady state. With this knowledge, the dew and bubble point were measured after certifying the steady state by checking the temperature agreement between S_1 and S_3 .

Measurement of Bubble and Condensation Points

At the start of the experiments, connecting tube C is attached. Cocks K_4 , K_5 , K_6 , and K_9 are opened and cocks K_2 , K_3 , K_7 , and K_8 are closed. The prepared solution of given composition is charged continuously from the feeder F, and the liquid is boiled in each still. In this experiment, the liquid in still S_2 overflows through branched tube O_3 .

The flow diagram is schematically shown in Fig. 2. The only material entering the region bounded by the dashed line in Fig. 2 is the feed F, while leaving the section is the overflow liquid from still S_2 .

By mass balance,

$$F = L_{S2} \quad (1)$$

$$Fx_F = L_{S2}x_{S2} \quad (2)$$

Substituting Eq.(1) into Eq.(2), gives

$$x_{S2} = x_F \quad (3)$$

where x_F and x_{S2} represent the feed composition and the composition of the overflow liquid from still S_2 , respectively.

Based on mass balance on still S_1 ,

$$F = L_{S1} \quad (4)$$

$$Fx_F = L_{S1}x_{S1} \quad (5)$$

Therefore,

$$x_{S1} = x_F \quad (6)$$

where L_{S1} and x_{S1} denote the overflow liquid from still S_1 and its composition, respectively.

Thus, the liquid compositions in the stills, x_{S1} and x_{S2} , must agree with the feed composition at steady state. Therefore, the temperatures obtained

Table 1 Physical properties of materials						
Material	Density at 25°C [g/cm ³]		Refractive index at 25°C		Boiling point, [°C]	
	Observed	Reported ¹⁵⁾	Observed	Reported ¹⁵⁾	Observed	Reported ¹⁵⁾
Benzene	0.8734	0.87367	1.4977	1.49790	80.16	80.105
Dioxane	1.0279	1.02802	1.4201	1.42025	101.12	101.320
Ethanol	0.7852	0.78508	1.3595	1.3596	78.31	78.325
Ethyl acetate	0.8947	0.89468	1.3702	1.37012 ^a	76.90	77.112
Methanol	0.7865	0.78655	1.3267	1.33057 ^b	64.53	64.501
^a at 25.2°C	^b at 15°C					

in stills S_1 and S_2 should equal the bubble point at the feed composition.

Likewise, making a mass balance on still S_3 ,

$$V_{S2} = L_{S3} \quad (7)$$

$$V_{S2}y_{S2} = L_{S3}x_{S3} \quad (8)$$

Combining Eq.(8) with Eq.(7), gives

$$x_{S3} = y_{S2} \quad (9)$$

where y_{S2} and x_{S3} represent the vapor composition in still S_2 and the liquid composition in still S_3 , respectively.

Thus the liquid composition in still S_3 must agree with the vapor composition in still S_2 , and the equilibrium liquid composition in S_2 equal the feed composition, as shown in Eq.(3). Therefore, the liquid composition in still S_3 equals the vapor composition, which is in equilibrium with the liquid of the feed composition. As a result, the temperature obtained in still S_3 should agree with the condensation point of feed composition, or the bubble point of the condensed equilibrium vapor for the liquid of feed composition. With this principle, the bubble and condensation points were measured after checking the agreement of temperatures registered in stills S_1 and S_2 for the certification of steady state.

In the present investigation, the solution of desired composition was prepared by mixing each pure substance, which was accurately weighed within ± 1 mg by use of an automatic balance. The amount of sample was about 300 cc in volume per determination. The period required for attainment of steady state lay between 15 and 45 minutes.

Materials

Reagents supplied by the Showa Chemical Co., Ltd., were used without further purification. The physical properties of the reagents used are listed in Table 1.

Experimental Results

Vapor-liquid equilibrium relationships were measured by the dew-bubble point method for methanol-dioxane and ethanol-dioxane systems at atmospheric pressure. For other systems, benzene-dioxane and ethyl acetate-dioxane, the bubble-condensation point method was used in the present investigation.

Table 2 Experimental dew and bubble point data at 760 mm of Hg pressure

Mole fraction of component(1)	System			
	Methanol(1)-Dioxane(2)		Ethanol(1)-Dioxane(2)	
	Dew point [°C]	Bubble point [°C]	Dew point [°C]	Bubble point [°C]
0.050	99.7	94.9	99.9	97.5
0.100	98.3	89.6	98.6	94.5
0.200	95.3	82.2	95.8	89.8
0.300	91.9	76.9	92.8	86.2
0.400	87.2	73.1	89.9	83.6
0.500	83.9	70.8	86.7	81.8
0.600	79.5	68.8	83.9	80.5
0.700	74.7	67.5	80.9	79.5
0.800	69.5	66.2	78.9	78.7
0.900	65.9	65.1	78.3	78.3
0.950	65.0	64.7	78.2	78.2

Table 3 Experimental bubble and condensation point data at 760 mm of Hg pressure

Mole fraction of component(1)	System			
	Benzene(1)-Dioxane(2)		Ethyl acetate(1)-Dioxane(2)	
	Bubble point [°C]	Condensation point [°C]	Bubble point [°C]	Condensation point [°C]
0.050	99.3	97.0	98.9	96.0
0.100	97.8	94.4	97.0	93.4
0.200	95.2	91.6	94.0	89.4
0.300	92.8	89.0	91.3	86.5
0.400	90.6	87.1	88.8	84.4
0.500	88.6	85.3	86.5	82.4
0.600	86.7	83.9	84.3	81.0
0.700	84.7	82.6	82.2	79.7
0.800	83.1	81.8	80.3	78.6
0.900	81.6	81.0	78.5	77.7
0.950	80.9	80.6	77.7	77.3

The experimental data obtained are presented in Tables 2 and 3. The experimental temperatures were corrected to the values at 760 mm of Hg pressure, by measuring the bubble point of water in the Swietoslawski ebulliometer¹⁴⁾ with the platinum resistance thermometer previously mentioned. The smoothed data obtained are listed in Table 4. Figs. 3 and 4 show the experimental results for the systems, methanol-dioxane and ethyl acetate-dioxane, respectively.

For the methanol-dioxane system, there was a relatively large difference between our data and previous data¹¹⁾, particularly in bubble points,

Table 4 Smoothed vapor-liquid equilibrium data at 760 mm of Hg pressure

System ^a								
I			II		III		IV	
x_1	y_1	t [°C]	y_1	t [°C]	y_1	t [°C]	y_1	t [°C]
0.000	0.000	101.1	0.000	101.1	0.000	101.1	0.000	101.1
0.050	0.212	94.9	0.137	97.5	0.132	99.3	0.122	98.9
0.100	0.365	89.6	0.245	94.5	0.220	97.8	0.221	97.1
0.200	0.542	82.2	0.403	89.8	0.360	95.2	0.376	94.1
0.300	0.657	76.9	0.519	86.2	0.476	92.8	0.500	91.3
0.400	0.735	73.1	0.610	83.6	0.577	90.6	0.600	88.8
0.500	0.779	70.7	0.666	81.8	0.668	88.6	0.688	86.5
0.600	0.818	68.8	0.716	80.5	0.753	86.6	0.762	84.4
0.700	0.850	67.5	0.765	79.4	0.824	84.7	0.832	82.3
0.800	0.892	66.2	0.826	78.7	0.883	83.1	0.894	80.4
0.900	0.947	65.1	0.904	78.3	0.943	81.6	0.950	78.5
0.950	0.974	64.7	0.950	78.2	0.973	80.9	0.975	77.7
1.000	1.000	64.5	1.000	78.3	1.000	80.2	1.000	76.9

^a System I: Methanol(1)-Dioxane(2) III: Benzene(1)-Dioxane(2)
 II: Ethanol(1)-Dioxane(2) IV: Ethyl acetate(1)-Dioxane(2)

Fig. 3 Methanol(1)-dioxane(2) system at 760 mm of Hg pressure

as shown in Fig. 3. The thermodynamic consistency of both equilibrium data were checked by the Herington area test³⁾; the positive and negative areas of the plots deviated 19.4 and 56.8% for our data and the previous data¹¹⁾, respectively. The vapor-liquid equilibrium relations were further measured by using the Smith-Bonner still; the equilibrium data obtained showed good agreement with the present data measured by the dew-bubble point method. As a result, our data can be considered correct and the previous data¹¹⁾ doubtful.

The average deviations of the smoothed data from the experimental data in all the systems measured

Fig. 4 Ethyl acetate(1)-dioxane(2) system at 760 mm of Hg pressure

were within 0.2°, 0.1°, and 0.1°C for the dew, bubble, and condensation point temperatures, respectively.

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Nomenclature

F = feed	[moles per minute]
L = liquid	[moles per minute]
t = temperature	[°C]
V = vapor	[moles per minute]

x = liquid composition [mole fraction]
 y = vapor composition [mole fraction]
 Subscripts
 1 = light component
 2 = heavy component
 S1 = still S_1 in Fig. 1
 S2 = still S_2 in Fig. 1
 S3 = still S_3 in Fig. 1

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PREDICTION OF HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA FOR MULTICOMPONENT SYSTEMS BY THE BWR EQUATION OF STATE*

MASAHIRO YORIZANE, SHOSHIN YOSHIMURA,
 HIROKATSU MASUOKA, MASANOBU NAKAMURA**

Department of Chemical Engineering, Hiroshima University, Hiroshima, Japan

A prediction method of high pressure vapor-liquid equilibria by the BWR equation of state is presented. This method in terms of ratio of mole fractions in liquid phase can be used more easily than the usual method, and is particularly useful for multicomponent system for which experimental data are not available. This method is shown to be successful in the prediction of the ternary methane-*n*-pentane system and quinary methane-ethane-propane-*n*-butane-*n*-pentane system.

For multicomponent systems few investigators have reported experimental data for vapor-liquid equilibrium constants. As for predictions or correlations of vapor-liquid equilibria for multicomponent systems, studies abound using the method of Chao-Seader^{3,10}), but the method of BWR based on the Benedict, Webb and Rubin equation of state is very scarce. In quaternary systems Nakahara and Hirata⁸) have reported on the existing region of vapor-liquid equilibria. According to their paper, when one needs a prediction for a quaternary system, estimation of the equilibrium compositions of binary and ternary systems is essential at the system temperature and pressure, and therefore the method is rather

tedious and time-consuming. In this paper we propose the easier method of prediction of multicomponent vapor-liquid equilibria by the BWR equation of state.

Usual Method

In n -component and two-phase systems the degree of freedom is equal to n , according to the phase rule. As shown in **Table 1**, when various sets of n phase variables are given, sets of remaining variables are necessarily specified⁹). This paper will examine case 5 in Table 1, which was not considered in reference⁹). When the pressure p , temperature T and the mole fractions in liquid phase $x_1, x_2, \dots, x_{n-2}$ (subscripts refer to the order of volatility in mixture) are selected as independent variables, the mole frac-

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