

New Apparatus for Isobaric Dew and Bubble Point Method

Methanol–Water, Ethyl Acetate–Ethanol, Water–1-Butanol, and Ethyl Acetate–Water Systems

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A new apparatus for isobaric vapor-liquid equilibrium measurements is proposed, based on the dew and bubble point method. Vapor-liquid equilibrium relationships were measured at atmospheric pressure for two miscible systems, methanol–water and ethyl acetate–ethanol. The immiscible systems measured were water–1-butanol and ethyl acetate–water. It is possible to measure vapor-liquid equilibrium relationships continuously throughout the composition range without analysis when using this equipment. The apparatus is especially useful for immiscible systems.

THE DEW and bubble point method is one way of measuring vapor-liquid equilibria. Investigators (6, 7, 8, 12, 14, 15, 17) have proposed several types of equipment based on this method, to determine the isothermal vapor-liquid equilibrium relationship. However, isobaric vapor-liquid equilibrium data are more important than isothermal data when calculating distillation problems.

A simple way of quickly determining isobaric vapor-liquid equilibrium relationships, based on the dew and bubble point method, is proposed.

EXPERIMENTAL APPARATUS

A unique apparatus for isobaric dew point measurements was proposed by Kojima *et al.* (10). It was based on an approximation principle (10), and the sample had to be analyzed.

Much work has been done on the measurement of isobaric bubble points and many ebulliometers have been proposed (3, 9, 11, 19, 22). However, it is necessary to correct the difference between the liquid composition at the steady state and the feed composition for holdup in the vapor space.

To eliminate these disadvantages a new apparatus was designed for the simultaneous measurement of isobaric dew and bubble points (Figure 1). It is constructed entirely of borosilicate glass. The main parts are two boiling flasks for the pure components, two vapor tubes, two three-way cocks, one mixing tube, ten thermometer pockets for dew point measurements, one flow-type ebulliometer, four condensers, and two receivers for measurement of flow rate.

The 2-liter boiling flasks are provided with electric heating units. Electric heaters are wound around the vapor tubes and the mixing tube. The flow-type ebulliometer (Figure 2) has a capacity of about 15 ml. Asbestos tapes cover the entire apparatus except the condensers. The heat to each part was varied by use of a slide regulator.

The dew and bubble point temperatures were measured by a mercury thermometer, calibrated to $\pm 0.1^\circ\text{C}$ in accordance with the standard platinum resistance thermometer in the Swietoslowski ebulliometer (19). The standard thermometer was calibrated in the National Research Laboratory of Metrology, Japan, according to the specifications of the international practical temperature scale (18).

PROCEDURE AND PRINCIPLE

First, the boiling flasks were filled with pure liquid and electric power was supplied to each heater. The three-way cocks were turned so that the pure vapors flowed into the mixing tube.

The saturated vapors, H_1 and H_2 , in the enthalpy-concentration diagram (Figure 3) are superheated to prevent partial condensation in the vapor tubes. The superheated vapor mixture indicated by M in Figure 3 is obtained throughout the mixing tube. In the temperature-heat loss diagram, the temperature curve bends at the dew point, D , as the specific heat is much less than the latent heat.

Based on the principle previously mentioned, the dew point would be determined by plotting the temperature

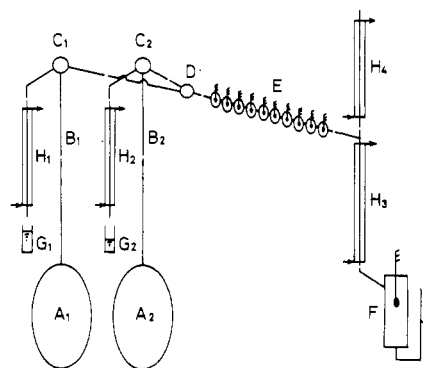


Figure 1. Schematic diagram of experimental equipment

- A. Boiling flasks of pure component
- B. Vapor tubes of pure component
- C. Three-way cocks
- D. Mixing tube
- E. Ten thermometer pockets for dew point measurements
- F. Flow-type ebulliometer
- G. Receivers for flow rate measurements
- H. Condensers

Table I. Physical Properties of Materials

Material	Density at 30° C, G/Cm ³		Refractive Index at 30° C		Boiling Point, ° C	
	Obsd.	Reported	Obsd.	Reported	Obsd.	Reported
Methanol	0.7819	0.7819 (1)	1.3245	...	64.59	64.75 (1)
1-Butanol	0.8058 ^c	0.80567 ^c (2)	1.3970 ^a	1.3970 ^a (2)	117.75	117.8 (2)
Ethyl acetate	0.8884	0.88830 (21)	1.3678	...	77.15	77.15 (21)
Ethanol	0.7809	0.78079 (23)	1.3590	...	78.38	78.36 (23)

^aAt 25° C.

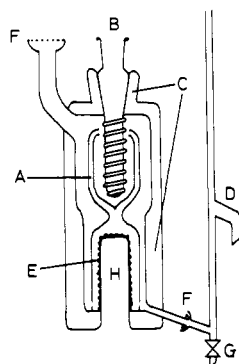


Figure 2. Flow-type ebulliometer

- A. Cottrell tube
- B. Thermometer well
- C. Evacuated jacket
- D. Overflow tube
- E. Glass dusts
- F. Ball joint
- G. Cock
- H. Heater tube

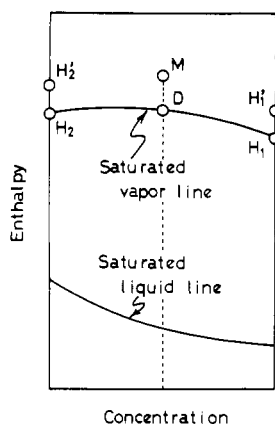


Figure 3. Enthalpy-concentration diagram

at each thermometer pocket and each position number, or by plotting the temperature at one thermometer pocket and the cutoff time of the heat to the mixing tube. In the present work, the latter method was used (Figure 4). The bubble points were measured in the flow-type ebulliometer to prevent deviation of the composition.

To measure the composition, both three-way cocks were turned so that the pure vapors condensed separately. Both amounts were accurately weighed within ± 1 mg with an automatic balance, and the composition was determined by the flow ratio.

A similar procedure was followed, after the composition was altered by changing the heat ratio between the boiling flasks. The time required was about 20 minutes per determination.

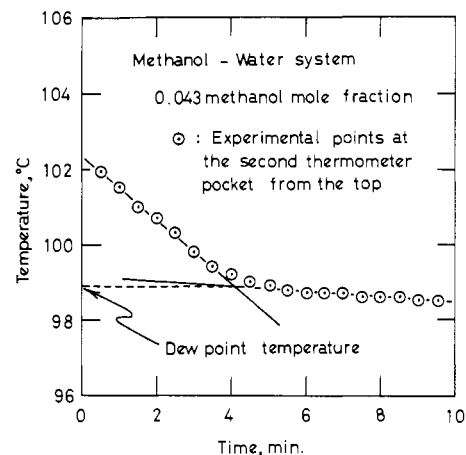


Figure 4. Determination of dew point temperatures

Table II. Original Data for Four Binary Systems Measured with New Equipment at 760 Mm of Hg

Component (A), Mole Fraction	Dew Point Temp., ° C	Bubble Point Temp., ° C	Component (A), Mole Fraction	Dew Point Temp., ° C	Bubble Point Temp., ° C
METHANOL (A)-WATER (B) SYSTEM					
0.043	98.8	92.8	0.456	86.7	74.0
0.109	97.3	86.9	0.610	80.9	71.3
0.206	94.7	81.2	0.753	74.3	68.6
0.348	90.5	76.8	0.900	68.5	66.1
ETHYL ACETATE (A)-ETHANOL (B) SYSTEM					
0.105	77.0	75.5	0.664	72.3	71.9
0.216	75.3	73.9	0.771	73.3	72.6
0.333	73.5	72.3	0.844	74.8	73.7
0.414	72.5	72.1	0.868	75.1	74.0
0.541	71.7	71.7	0.917	75.8	74.9
WATER (A)-1-BUTANOL (B) SYSTEM					
0.075	115.8	109.3	0.744	93.0	92.4
0.189	112.6	101.6	0.767	92.9	92.3
0.271	110.6	97.9	0.827	94.8	92.3
0.357	107.9	95.0	0.892	97.5	92.3
0.434	105.6	93.7	0.957	99.0	92.3
0.526	102.2	92.8	0.983	99.5	93.6
0.615	99.1	92.4	0.995	99.9	97.3
0.697	95.7	92.3			
ETHYL ACETATE (A)-WATER (B) SYSTEM					
0.00066	...	91.9	0.333	88.0	70.4
0.00143	...	87.9	0.446	84.2	70.4
0.00324	...	83.0	0.587	78.4	70.4
0.00757	...	76.6	0.614	76.5	70.5
0.00978	...	73.7	0.694	71.2	70.5
0.023	...	71.2	0.707	70.9	70.4
0.084	96.4	70.4	0.753	72.4	70.5
0.092	96.5	70.4	0.797	73.3	70.7
0.159	94.3	70.4	0.834	74.3	71.0
0.218	92.4	70.4	0.920	75.8	72.8
0.275	90.4	70.5	0.936	76.1	73.3

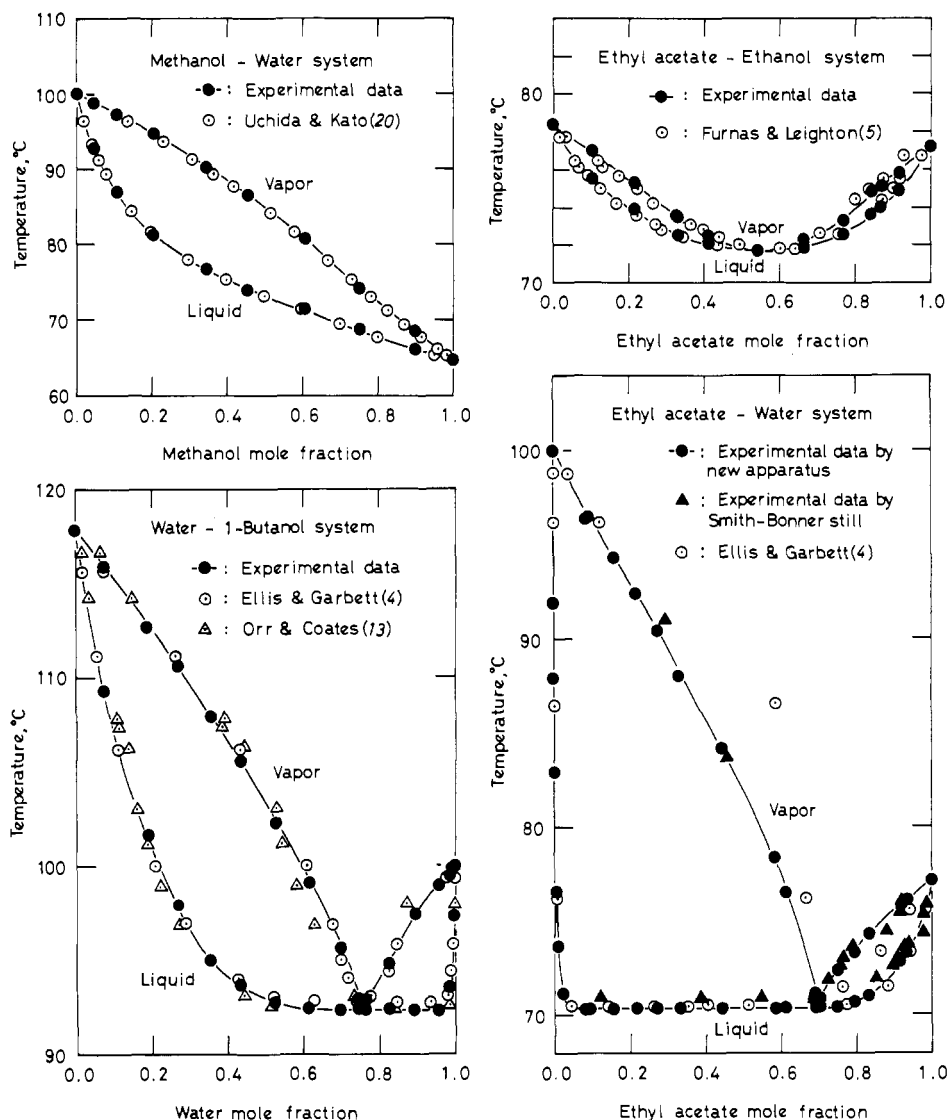


Figure 5. Temperature-composition diagrams of four binary systems at 760 mm of Hg

MATERIALS AND RESULTS

All reagents (Showa Chemical Co., Ltd.) except methanol were further purified by fractionation. The final physical properties of the materials used are listed in Table I.

The vapor-liquid equilibrium relationships were measured with the new equipment. The experimental data are presented in Table II and Figure 5, together with previous data measured by circulating stills. The experimental temperatures were corrected to the values of 760 mm of Hg, by measuring the boiling points of water in the Swietoslowski ebulliometer (19) with the platinum resistance thermometer previously mentioned. In the ethyl acetate-water system, five bubble points within 0.01 mole fraction of ethyl acetate were measured by continuously supplying liquid of known composition from the top of the condenser to the flow-type ebulliometer. Smoothed data are presented in Table III, and vapor-liquid composition diagrams are shown in Figure 6 together with previous data.

In the methanol-water system, our data agreed well with previous data (20) (Figures 5 and 6). In the ethyl acetate-ethanol system, the difference between our data and previous data (5) was relatively large. In the water-1-butanol

system, our data differed slightly from previous data (4, 13).

In the ethyl acetate-water system, there was a relatively large difference between our data and previous data, particularly in the dew points (Figure 5). The system was also measured with the Smith-Bonner still (16) and data are presented in Table IV and Figures 5 and 6. In the experiments, the vapor and liquid samples were analyzed by gas chromatography. As a result, our data obtained by the new equipment agreed well with our data measured by the Smith-Bonner still rather than the previous data (4).

The average deviations of the smoothed data from the experimental data in all the systems measured were 0.11° and 0.05°C for the dew and bubble points, respectively.

ACKNOWLEDGMENT

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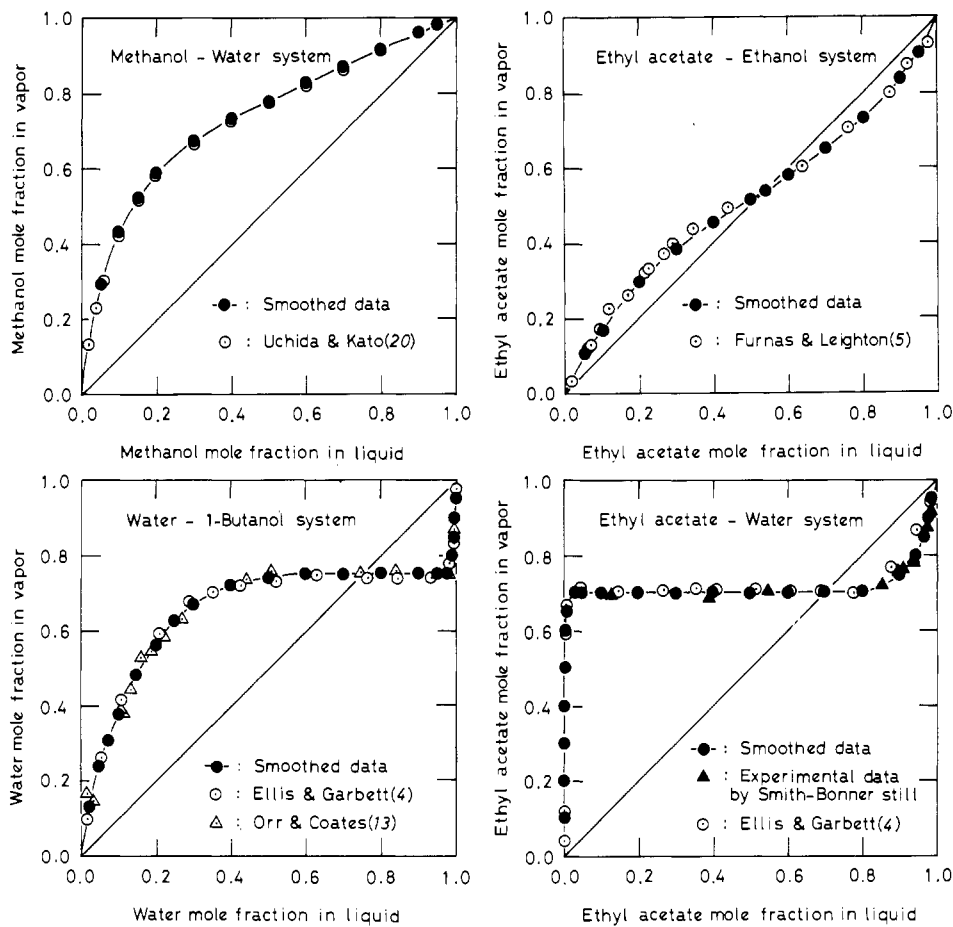


Figure 6. Vapor-liquid composition diagrams of four binary systems at 760 mm of Hg

Table III. Smoothed Data for Four Binary Systems Taken with New Apparatus at 760 Mm of Hg

Temp., °C	Component (A), Mole Fraction		Temp., °C	Component (A), Mole Fraction		Temp., °C	Component (A), Mole Fraction		Temp., °C	Component (A), Mole Fraction	
	Liquid	Vapor		Liquid	Vapor		Liquid	Vapor		Liquid	Vapor
METHANOL (A)-WATER (B) SYSTEM											
100.0	0.000	0.000	73.2	0.500	0.783						
92.2	0.050	0.293	71.4	0.600	0.831						
87.5	0.100	0.435	69.6	0.700	0.874						
84.3	0.150	0.522	67.8	0.800	0.918						
81.5	0.200	0.590	66.1	0.900	0.961						
78.0	0.300	0.675	65.4	0.950	0.981						
75.4	0.400	0.735	64.6	1.000	1.000						
ETHYL ACETATE (A)-ETHANOL (B) SYSTEM											
78.4	0.000	0.000	71.7	0.541	0.541						
77.0	0.050	0.106	71.8	0.600	0.580						
75.7	0.100	0.183	72.1	0.700	0.651						
74.0	0.200	0.300	73.0	0.800	0.735						
72.8	0.300	0.387	74.6	0.900	0.837						
72.1	0.400	0.456	75.7	0.950	0.907						
71.8	0.500	0.516	77.2	1.000	1.000						
WATER (A)-1-BUTANOL (B) SYSTEM											
117.8	0.000	0.000	92.4	0.600	0.752						
114.2	0.025	0.132	92.3	0.700	0.754						
111.4	0.050	0.239	92.3	0.800	0.754						
109.3	0.075	0.311	92.3	0.900	0.754						
WATER (A)-1-BUTANOL (B) SYSTEM (Contd.)											
107.2	0.100	0.380	92.3	0.950	0.754						
103.8	0.150	0.483	92.3	0.975	0.754						
101.0	0.200	0.563	94.2	0.988	0.800						
98.6	0.250	0.626	96.0	0.992	0.850						
96.6	0.300	0.671	97.4	0.995	0.900						
94.3	0.400	0.722	98.8	0.998	0.950						
93.1	0.500	0.741	100.0	1.000	1.000						
ETHYL ACETATE (A)-WATER (B) SYSTEM											
100.0	0.00000	0.000	70.4	0.300	0.701						
96.5	0.00024	0.100	70.4	0.400	0.701						
92.9	0.00055	0.200	70.4	0.500	0.701						
89.5	0.00105	0.300	70.4	0.600	0.701						
85.9	0.00201	0.400	70.4	0.700	0.701						
82.1	0.00370	0.500	70.7	0.800	0.705						
77.5	0.00683	0.600	72.2	0.900	0.750						
74.3	0.00935	0.650	73.5	0.941	0.800						
70.5	0.030	0.700	74.5	0.965	0.850						
70.4	0.050	0.701	75.5	0.975	0.900						
70.4	0.100	0.701	76.3	0.988	0.950						
70.4	0.200	0.701	77.2	1.000	1.000						

Table IV. Experimental Data for Ethyl Acetate (A)-Water (B) System Taken from Smith-Bonner Still at 760 Mm of Hg

Temp., °C	Ethyl Acetate, Mole Fraction		Temp., °C	Ethyl Acetate, Mole Fraction	
	Liquid	Vapor		Liquid	Vapor
91.0	...	0.297	73.0	0.908	0.765
83.7	...	0.459	73.5	0.934	0.791
70.9	0.124	0.693	73.6	0.934	0.788
70.9	0.385	0.688	73.7	0.939	0.787
70.9	0.548	0.710	74.4	0.974	0.876
71.9	0.851	0.724	75.4	0.978	0.911
72.6	0.894	0.757	75.9	0.986	0.917

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Terephthalic Acid Solubility

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The solubility of terephthalic acid was determined in toluene, anisole, 3-pentanone, and 1,4-dioxane. It correlates with the Brønsted basicity of the solvents previously correlated by an infrared spectral shift technique.

TEREPHTHALIC acid, which finds extensive use in poly(ethylene terephthalate) films and fibers, is one of the most intractable organic compounds (10). Its high melting point [triple point, 427°C (10)] is consistent with its low solubility (1, 2, 10) in nonbasic solvents. Since most organic reactions are carried out in solution, the ability to predict the solubility of terephthalic acid would be very useful. We have determined its solubility in several organic solvents, and report a scheme which allows the solubility to be estimated.

EXPERIMENTAL

The terephthalic acid was 99.98% pure. The chief impurity was toluic acid (140 ppm). The solvents were reagent grade.

The solubilities were determined by weighing the terephthalic acid and solvent into a glass tube, which was sealed and submerged in a constant temperature bath thermostated to $\pm 0.05^\circ\text{C}$. The bath temperature was raised 1°C per 10 minutes and the tube was shaken until all the acid was dissolved (5, 11).

RESULTS AND DISCUSSION

The solubilities of terephthalic acid in toluene, anisole, 3-pentanone, 1,4-dioxane, and *N,N*-dimethylformamide are given in Table I. When the log of the mole fraction of terephthalic acid is plotted against the reciprocal of the temperature, a straight line is obtained for each solvent (4), with correlation coefficients of 0.98 or better. Thus, the solubilities at other temperatures may be reliably obtained by extrapolation.

The solubility of some organic acids has been correlated with the dielectric constant of the solvent (6), but no such correlation exists for terephthalic acid. Dioxane and toluene have similar dielectric constants (9), but differ greatly in their ability to dissolve terephthalic acid.

Since terephthalic acid dissolves readily in basic media, it seemed possible that its solubility in any solvent might correlate with the Brønsted basicity—i.e., the proton-accepting ability of the solvent. Recently this property was correlated for a number of organic solvents at 25° (3, 7) by measuring the shift, $\Delta\nu$, of the infrared stretching frequency of methanol-*D* in a given solvent from its position in benzene.