A NEW EXPERIMENTAL METHOD OF VAPOR-LIQUID EQUILIBRIA AT HIGH PRESSURES

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A new experimental method of vapor-liquid equilibria at high pressures for binary systems which requires no analysis of phase compositions is proposed in the present study. The equilibrium vapor and liquid compositions can be evaluated by combining a couple of data at the same temperature and pressure, based on mass balance and the phase rule. A new apparatus for vapor-liquid equilibria at high pressures was constructed for use with the present experimental method. Vapor-liquid equilibria and saturated densities at high pressures were measured for the carbon dioxide–acetone system at 298.15 K. The experimental data obtained were correlated with the pseudocubic perturbed hard-sphere equation of state proposed previously.

Introduction

Vapor-liquid equilibrium relations are required in the practical use, such as in the design and operation of distillation equipment. Several experimental methods of vapor-liquid equilibria are available in literature. In the conventional experimental methods, the compositions both of the vapor and of the liquid are analytically determined after attainment of equilibrium state.

The dew-bubble point method does not require the sampling of liquid or vapor for analysis. This is a big advantage on the measurement of vapor-liquid equilibria. The authors[6-9] previously proposed the dew-bubble point temperature method and its apparatus.

The saturated volume method was investigated by Hill[3], Newman *et al.*[14], Redewald *et al.*[20], and DiAndreth *et al.*[1,2]. As a great advantage, the saturated volume method does not require any analytical instrument for vapor-liquid equilibrium measurements. The saturated vapor and liquid densities can be further evaluated, based on phase rule. In the saturated volume method, the saturated vapor and liquid volumes should be measured. The precise measurement of saturated volumes both of vapor and of liquid seems however troublesome for the practical experiment.

Parrish[17-20] and Takac *et al.*[23] have introduced the Mettler Parr vibrating-tube density meter for PVT measurement of liquids. Nagarajan *et al.*[4,12,13], Panagiotopoulus *et al.*[16], and Sandler *et al.*[11,21,22] have recently used the vibrating-tube density meters in their vapor-liquid equilibrium apparatus of circulation method. The equilibrium compositions of vapor and liquid were determined by gas chromatography. The saturated densities of vapor and of liquid were further measured with the density meters.

In the present study, a new experimental method of vapor-liquid equilibria at high pressures for binary systems is proposed, applying the density meters effectively. The present experimental method does not require any analysis of phase compositions. In the proposed experimental method, not only the equilibrium vapor and liquid compositions but also the saturated densities of vapor and of liquid can be obtained. The present experimental method seems essentially new.

1. Experimental

1.1 Experimental principles

The present experimental method requires a high-pressure apparatus equipped with two density meters. The method is based on the phase rule and mass balance. The equilibrium condition for binary vapor-liquid equilibria is fixed by giving the temperature and pressure, as the degree of freedom is two.

With a couple of data at the same temperature and pressure, the following equations are easily obtained, based on mass balance and the phase rule.

For the first experiment,

$$W=\rho_v V_v+\rho_l V_l \tag{1}$$

$$WX_f=\rho_v V_v Y+\rho_l V_l X \tag{2}$$

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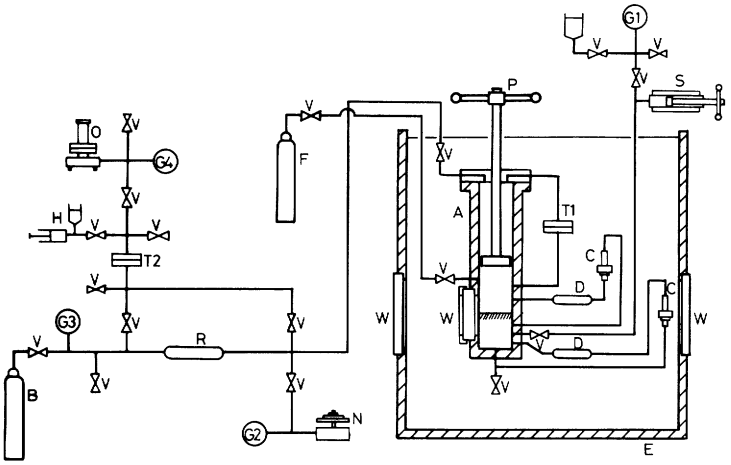

Fig. 1. Schematic diagram of apparatus for the new experimental method of vapor-liquid equilibria
A, Cell; B, Nitrogen Bomb; C, Circulation Pump; D, Density Meter; E, Constant-Temperature Liquid Bath; F, Gas Bomb; G, Pressure Gage; H, Hand Pump; N, Air Dead-Weight Gage; O, Oil Dead-Weight Gage; P, Piston; R, Surge Tank; S, Hand Pump Syringe; T, Pressure Transducer; V, Valve; W, Visual Window

$$V_t = V_v + V_l \tag{3}$$

For the second experiment,

$$W^* = \rho_v V_v^* + \rho_l V_l^* \tag{4}$$

$$W^* X_f^* = \rho_v V_v^* Y + \rho_l V_l^* X \tag{5}$$

$$V_t^* = V_v^* + V_l^* \tag{6}$$

where, W, V, X, Y, and ρ, respectively, denote the feed weight, volume, liquid weight fraction, vapor weight fraction, and density. The subscripts "v", "l" and "t" are the vapor phase, liquid phase, and their total, respectively; "f" represents the feed. The superscript "*" denotes the second-run data at the same temperature and pressure.

The equilibrium vapor and liquid compositions, X and Y, can be derived from Eqs. (1) to (6) as follows:

$$X = \frac{WX_f - \rho_v V_v Y}{\rho_l V_l} \tag{7}$$

$$Y = \frac{W^* X_f^* - (V_l^*/V_l) W X_f}{\rho_v [V_v^* - (V_l^*/V_l) V_v]} \tag{8}$$

where

$$V_v = \frac{W - \rho_l V_t}{\rho_v - \rho_l}, \quad V_v^* = \frac{W^* - \rho_l V_t^*}{\rho_v - \rho_l} \tag{9}$$

$$V_l = \frac{\rho_v V_t - W}{\rho_v - \rho_l}, \quad V_l^* = \frac{\rho_v V_t^* - W^*}{\rho_v - \rho_l} \tag{10}$$

Based on Eqs. (7) to (10), the equilibrium vapor and liquid weight fraction, X and Y, can be obtained from a couple of data on the feed weight W, feed weight fraction X_f, total volume V_t, and the densities of the vapor and liquid phases, ρ_v and ρ_l. The present experimental method does not require any analysis of phase compositions. The total volume V_t, is measured, but there is no need for each phase volume, V_v and V_l.

In the conventional method of vapor-liquid equilibrium measurement, the vapor and liquid are withdrawn from the equilibrium cell after atainment of equilibrium state, and the vapor and liquid compositions are determined by an analytical instrument in general. The sampling and analysis of equilibrium phases are, however, often troublesome, especially for high-pressure vapor-liquid equilibria.

The present experimental principles can be applied for phase equilibrium measurement of ternary systems. For vapor-liquid equilibria of ternary systems, two sets of data at the same temperature, pressure, vapor density, and liquid density are required. The actual experiments, however, seem troublesome. For vapor-liquid-liquid equilibria of ternary systems, six sets of data are required in principle. The experiments seem very troublesome. The present experimental principles cannot be applied for vapor-liquid-liquid equilibria in binary systems.

1.2 Experimental apparatus

The new apparatus, built for a maximum temperature and pressure of 400 K and 20 MPa, is schematically shown in **Fig. 1**. The main parts of the apparatus are a cell A, position P, air dead-weight gage N, oil dead-weight gage 0, hand pump syringe S, density meters D, circulation pumps C, gas bomb F, and pressure transducers T. The apparatus is placed in a constant-temperature liquid bath E controlled within ± 0.01 K. The volume of the lower space in the cell A is variable for 78 cm^3 to 134 cm^3 by the motion of the piston P with a sensitivity of 0.01 cm^3. The accuracy of the volume seems about ± 1 cm^3. The meters used in the present apparatus and their accuracies are shown in **Table 1**.

Table 1. Meters used in the present apparatus

Meters	Type	Pressure range	Accuracy
Density meter	Anton Paar DMA512	0–40 MPa	0.1 kg/m^3
Thermometer	Heweltt Packard 2804A		Resolution 0.0001 K
Pressure gage	Ruska 2465–752 (Air DWG)	0.014–7 MPa	0.01%
	2480–700 (Oil DWG)	0.2–103 MPa	0.01%
Pressure transducer	Ruska 2439–702 (Usual type)	–7 MPa	50 ppm
	2413–705 (High temp.)	–103 MPa	5 ppm

Table 2. Experimental data for carbon dioxide-acetone system at 298.15 K

Pressure [MPa]	Density [kg/m^3] Liquid	Vapor	Mole fraction of CO_2 Liquid	Vapor
2.153	838.5	44.1	0.380	0.978
2.556	847.2	53.7	0.445	0.979
3.017	856.1	66.0	0.517	0.980
3.368	861.4	75.6	0.573	0.979

1.3 Experimental procedures

At the start of the experiment, the gas of the first component is charged into the cell after the evacuation of cell A. The pressure difference between the upper and lower spaces is kept null. The temperature and pressure are measured. The volume is determined by the motion of the piston P. The amount of the first component is evaluated from the volume and density. The liquid of the second component is charged with the hand pump syringe S to the cell. The amount of the second component is evaluated from the movement of the hand pump syringe S with a sensitivity of 0.01 cm^3. The accuracy of feed composition seems about ± 0.0003 weight fraction.

The vapor and liquid phases are both circulated. The apparatus is vibrated with a motor to achieve equilibrium. The pressure difference between the upper and lower spaces in cell A is maintained null with the piston P. After attainment of equilibrium the densities of vapor and liquid, pressure, and temperature are measured, observing the coexistence of vapor and liquid phases through the glass window W. The total volume is further evaluated by the movement of the piston P.

The second experiment is done at the same temperature and pressure, at different feed composition. Combining the couple of data at the same temperature and pressure, the equilibrium vapor and liquid compositions are calculated by Eqs. (7) to (10).

2. Results

The equilibrium compositions and saturated densities were measured for the carbon dioxide-acetone system at 298.15 K. Carbon dioxide was supplied by Nihon Sanso Co. Ltd. with the guarantee of 99.9 percent purity. Acetone was the special-grade reagent of Wako Pure Chemicals Co. Ltd. The experimental saturated-phase densities and vapor-liquid equilibria are given in **Table 2** and **Figs. 2** and **3**. The equilibrium vapor and liquid compositions were

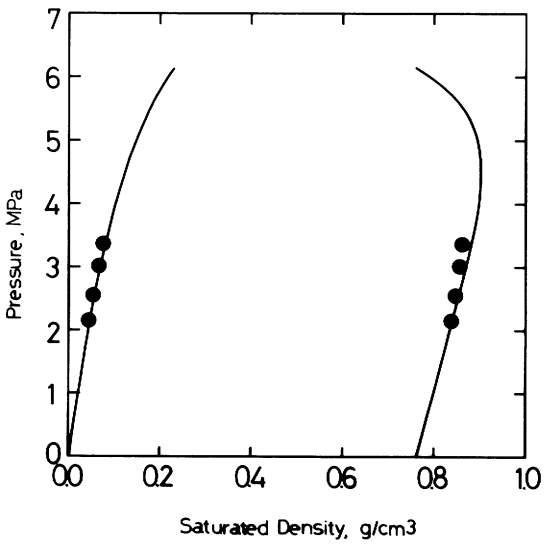

Fig. 2. Experimental saturated vapor and liquid densities for carbon dioxide-acetone system at 298.15 K
●, experimental; —, correlated with EOS

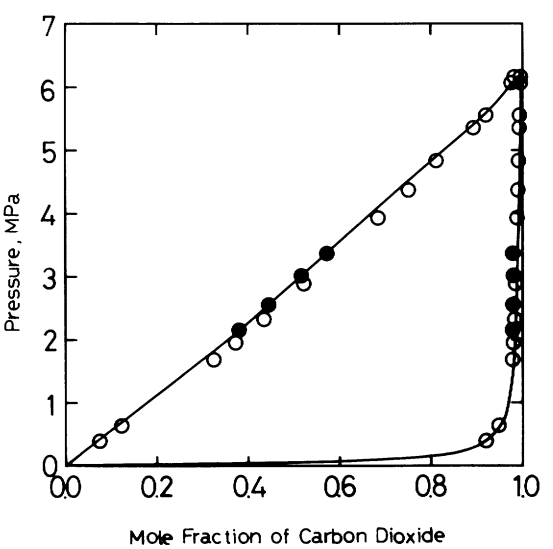

Fig. 3. Experimental vapor-liquid equilibrium relations for carbon dioxide-acetone system at 298.15 K
●, experimental; ○, Katayama *et al.*[5]; —, correlated with EOS

calculated from Eqs. (7) to (10). The accuracies of the calculated vapor and liquid compositions seem to be about 0.005 and 0.001 mole fraction respectively. In Fig. 3, solid and open circles denote the present experimental data and the previous data of Katayama *et al.*[5] respectively. Saturated vapor and liquid density data for this system are not available in the literature.

The experimental vapor-liquid equilibria were correlated with the following equation of state previously proposed by the authors[10].

$$P=\frac{RT}{v^0-b}-\frac{a}{(v^0+m)(v^0-n)} \tag{11}$$

where

$$\frac{v^0}{v}=4v+\frac{(1-v)^3}{1+v+v^2-v^3},\quad v=\frac{b}{4v} \tag{12}$$

in which

$$a=K_a\cdot a_c,\quad a_c=\Omega_a\frac{(RT_c)^2}{P_c} \tag{13}$$

$$b=\Omega_b\frac{RT_c}{P_c} \tag{14}$$

$$m=\Omega_m\frac{RT_c}{P_c},\quad n=\Omega_n\frac{RT_c}{P_c} \tag{15}$$

$$\Omega_a=(1-\alpha)^3,\quad \Omega_b=Z_c \tag{16}$$

$$\Omega_m=\frac{1-\alpha}{2}(\sqrt{1-4\alpha}+1)-(\alpha+Z_c) \tag{17}$$

$$\Omega_n=\frac{1-\alpha}{2}(\sqrt{1-4\alpha}-1)+(\alpha+Z_c) \tag{18}$$

$$\alpha=(27/83)Z_c \tag{19}$$

where

$$K_a=1-S(1-T_r^{2/3}) \tag{20}$$

$$S=\frac{1-K_a^{nb}}{1-(T_r^{nb})^{2/3}}-0.0017\cdot\mu_r^2\cdot\Delta T_r \tag{21}$$

$$\mu_r^2=\mu^2/[9.8694\cdot10^{-5}(RT_c)^2/P_c] \tag{22}$$

$$\Delta T_r=T_r-T_r^{nb} \tag{23}$$

Given temperature and pressure, the pseudocubic perturbed hard-sphere equation of state has at most three real roots for volume. The equation of state strictly satisfies the critical point requirements.

In the present study, the following mixing rules, similar to those of Ozawa *et al.*[15], were introduced for the application of the equation of state to mixtures.

$$a=\sum_i\sum_j x_ix_ja_{ij},\quad a_{ij}=(1-k_{ij})\sqrt{a_ia_j} \tag{24}$$

Table 3. Correlation results of vapor-liquid equilibria with equation of state

Parameters		Saturated density [kg/m^3]		Mole fraction	
k_{12}	l_{12}	$\lvert\Delta\rho_l\rvert_{av}$	$\lvert\Delta\rho_v\rvert_{av}$	$\lvert\Delta x_1\rvert_{av}$	$\lvert\Delta y_1\rvert_{av}$
0.0193	−0.0157	9.6	3.0	0.001	0.008

$\lvert\Delta\rho_l\rvert_{av}$: average absolute difference of saturated liquid density
$\lvert\Delta\rho_v\rvert_{av}$: average absolute difference of saturated vapor density
$\lvert\Delta x_1\rvert_{av}$: average absolute difference of liquid mole fraction
$\lvert\Delta y_1\rvert_{av}$: average absolute difference of vapor mole fraction

$$b^{1/3}=\sum_i\sum_j x_ix_jb_{ij}^{1/3} \tag{25}$$

$$b_{ij}^{1/3}=(1-l_{ij})(b_i^{1/3}+b_j^{1/3})/2 \tag{26}$$

$$m^{1/3}=\sum_i\sum_j x_ix_jm_{ij}^{1/3} \tag{27}$$

$$m_{ij}^{1/3}=(1-l_{ij})(m_i^{1/3}+m_j^{1/3})/2 \tag{28}$$

$$n^{1/3}=\sum_i\sum_j x_ix_jn_{ij}^{1/3} \tag{29}$$

$$n_{ij}^{1/3}=(1-l_{ij})(n_i^{1/3}+n_j^{1/3})/2 \tag{30}$$

where "k_{ij}" and "l_{ij}" are the binary interaction parameters.

The pseudocubic perturbed hard-sphere equation of state was applied to the correlation of the experimental high pressure vapor-liquid equilibria. Calculated results are shown in **Table 3**. In the present calculations, the following objective function was used to obtain the binary interaction parameters "k_{ij}" and "l_{ij}" in the mixing rules.

$$\text{O.F.}=\sum_1^N[\lvert x_{\text{calc}}-x_{\text{expl}}\rvert+\lvert y_{\text{calc}}-y_{\text{expl}}\rvert]^2 \tag{31}$$

where x and y indicate the liquid and vapor mole fractions, respectively.

The curves in Figs. 2 and 3 show the calculated results with the pseudocubic perturbed hard-sphere equation of state, giving satisfactory agreement with the experimental ones.

Conclusion

A new experimental method of binary vapor-liquid equilibria at high pressures is proposed. It requires no analysis of phase compositions. The equilibrium vapor and liquid compositions can be evaluated from a couple of data at the same temperature and pressure, based on mass balance and the phase rule. An experimental apparatus for binary vapor-liquid equilibrium measurements was constructed for the new experimental method. The vapor-liquid equilibria and saturated densities were measured for the carbon dioxide-acetone system at 298.15 K.

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Nomenclature

a, b, m, n	=	parameters in EOS	
k, l	=	binary interaction parameters	[—]
K_a	=	correction factor defined by Eq. (13)	[—]
N	=	number of data points	[—]
P	=	pressure	[kPa]
R	=	gas constant	[kPa·m^3/kmol·K]
S	=	parameter given by Eq. (21)	[—]
T	=	temperature	[K]
V	=	volume	[m^3]
v	=	molar volume	[m^3/kmol]
W	=	amount of feed	[kg]
X	=	liquid weight fraction	[—]
x	=	liquid mole fraction	[—]
Y	=	vapor weight fraction	[—]
y	=	vapor mole fraction	[—]
Z	=	compressibility factor	[—]
α	=	parameter given by Eq. (19)	[—]
Δ	=	difference	
μ	=	dipole moment	[debyes]
ν	=	volume function given by Eq. (12)	[—]
ρ	=	density	[kg/m^3]
$\Omega_a, \Omega_b, \Omega_m, \Omega_n$	=	dimentionless parameters	[—]

〈Subscripts〉

c	=	critical state property
calc	=	calculated
expl	=	experimental
f	=	feed
i, j	=	components
l	=	liquid phase
r	=	reduced property
t	=	total
v	=	vapor phase
1, 2	=	components

〈Superscripts〉

nb	=	normal boiling point
0	=	apparent value
*	=	second run

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