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Dew- and Bubble-Point Measurements for the Mixtures of Dichlorodifluoromethane and Bromotrifluoromethane[1]

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The dew and bubble points for the mixtures of dichlorodifluoromethane (CCl_2F_2; R 12) and bromotrifluoromethane ($CBrF_3$; R 13B1) were measured with the use of a constant-volume method coupled with an expansion procedure and visual observation of the meniscus at the vapor–liquid interface. In order to check the reliability of the apparatus used, vapor pressure measurements were conducted for carbon dioxide at 273.15 K and for two pure components, CCl_2F_2 and $CBrF_3$. Thirty-eight dew and bubble points of the $CCl_2F_2 + CBrF_3$ system were determined for four different compositions of 0, 21, 45, and 70 mol% $CBrF_3$ in the range of temperatures from 299 to 384 K, pressures up to 4.2 MPa, and densities from 89 to 1228 $kg \cdot m^{-3}$.

KEY WORDS: bromotrifluoromethane; bubble point; dew point; dichlorodifluoromethane; mixtures of refrigerants; vapor–liquid equilibria.

1. INTRODUCTION

The accurate measurement of the vapor–liquid equilibria for mixtures of refrigerants has become of interest because of their application in vapor compression cycles for refrigeration. The binary system of dichlorodifluoromethane (CCl_2F_2) and bromotrifluoromethane ($CBrF_3$) is considered to be one such technically important mixture of refrigerants. Pure CCl_2F_2 and $CBrF_3$ are designated R 12 and R 13B1 in ASHRAE nomenclature. Their thermodynamic properties as pure substances have

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been extensively investigated by many workers until now. However, no experimental data on the vapor–liquid equilibria for the concerned system are presently available. In the present paper, experimental work on the dew and bubble point for the binary system $CCl_2F_2 + CBrF_3$ is reported. In addition, available prediction methods are compared with the present experimental data.

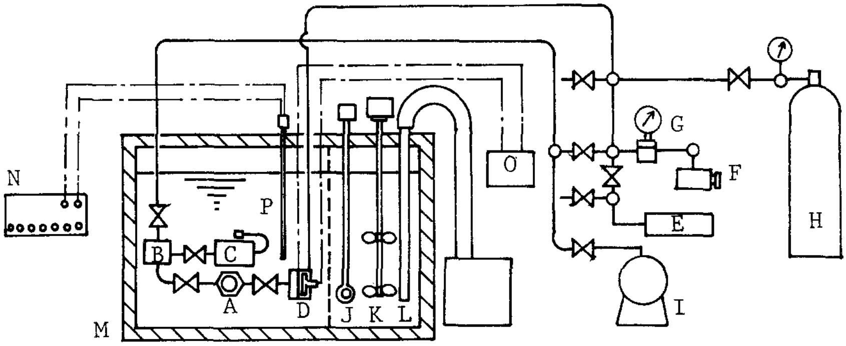
2. EXPERIMENTAL

2.1. Method

The dew- and bubble-point method was selected for investigating high-pressure vapor–liquid equilibria in this work. The sampling analysis of the separate phases in the sample cell was eliminated. The measurements consist of a series of pressure–volume–temperature–composition ($PVTx$) data obtained for the isochore at a constant composition with pressure and temperature as the variables. The temperature and the pressure at the dew or bubble point were determined from the P–T curve for each isochore when constant-volume measurements were conducted. In the constant-volume method the density is determined from the known mass of the sample in the cell and the cell volume. However, this method cannot be used when the isochoric slope does not change abruptly during the phase transition, as is the case near the maximum temperature in the P–T dew–bubble loop at constant x. In order to solve this, the sample cell was made as an optical cell with two sapphire windows, through which we can observe the disappearance or the reappearance of the meniscus at the vapor–liquid interface. The expansion procedure, as performed in the Burnett method of volumetric measurement [1], was combined with the constant-volume method and the meniscus observation to obtain successively the dew and bubble points for a series of densities at fixed composition.

2.2. Apparatus and Procedure

The experimental apparatus is shown schematically in Fig. 1. The design concept is similar to those of Okazaki *et al.* [2] and Takaishi *et al.* [3]. The optical cell has two synthetic sapphire windows (17 mm in thickness) through which the meniscus observation can be carried out. The sample can be expanded into the expansion vessel, which is connected to the optical cell. The supply vessel is also connected to the expansion vessel. These vessels were made of 304 stainless steel except for the Teflon "O" rings used to seal the sapphire windows in the optical cell. The inner



A:Optical cell
B:Expansion vessel
C:Supply vessel
D:Differential pressure detector
E:Digital pressure gage
F:Pressure controller
G:Bourdon pressure gage
H:Nitrogen cylinder
⋈:High pressure valves

I:Vacuum pump
J:Electric heater
K:Stirrer
L:Cooler
M:Thermostated bath
N:Resistance thermometer bridge
O:Electronic device for detecting differential pressure
P:Platinum resistance thermometer

Fig. 1. Schematic setup of the apparatus.

volumes of the optical cell, the expansion vessel, and the supply vessel were 21.580 ± 0.010, 7.261 ± 0.010, and $101.771 \pm 0.010\ cm^3$, respectively; these values were obtained by calibrating with water of a known density at 293.15 K and 101.325 kPa.

For the preparation of the sample, two pure components are carefully filled in the two separate vessels, which have been preevacuated. The mass of the pure component in each vessel is adjusted to the prescribed mass and then weighed with a precise chemical balance whose sensitivity is 2 mg. Then the two pure components in the separate vessels are charged one by one into the supply vessel cooled by liquid nitrogen. The supply vessel is then connected to the expansion vessel, as shown in Fig. 1. After evacuation of the expansion vessel and the optical cell, the mixture sample in the supply vessel is transferred into both of them. Then the constant-volume measurement and the meniscus observation with the use of the optical cell are carried out for the initial isochore. The dew- and bubble-point measurements are repeated for several isochores obtained by expanding the sample from the optical cell into the expansion vessel. Those expansions are usually performed at a state where the sample is kept under the homogeneous phase at a constant temperature. If a phase separation occurs during the sample charge and expansion, the temperature of the sample is raised gradually and kept constant so far as the meniscus disappears completely. During that time, three vessels are rocked to rehomogenize the sample density and composition.

The temperature measurements were conducted with the use of a resistance thermometer bridge (Tinsley Type 5840) and a platinum resistance thermometer calibrated with a precision of ±5 mK on IPTS-68 at the National Research Laboratory of Metrology, Ibaraki, Japan. The bath-fluid temperature was controlled within a fluctuation of ±10 mK during the experiment.

The pressure of the sample in the optical cell was measured by balancing it with pressurized nitrogen in an external system through a stainless membrane (30 μm in thickness) of a differential pressure detector with a sensitivity of 0.1 kPa. The pressure of nitrogen was measured with the use of a precise digital pressure gage (Nagano Keiki Seisakusho Type GC-11), which had been previously calibrated with a precision of ±2 kPa with respect to the reference pressure generated by an air piston gage (Ruska Model 2465). Prior to the main experiment, the accuracy of this pressure measuring system was examined with the use of the vapor pressure of carbon dioxide at 273.15 K and 3.4850 MPa [4], where 3.485 MPa was observed.

The purity of the samples used to prepare the mixture sample was 99.99 mol% for CCl_2F_2 and 99.96 mol% for $CBrF_3$.

3. RESULTS

3.1. Vapor Pressures for Pure Components

Measurements of the vapor pressure with this apparatus provide a cross-check of the previously reported data, of the purity of the sample used, and of the reliability of the apparatus itself. Thus the vapor pressures of CCl_2F_2 and $CBrF_3$ were measured and are given in Table I. Figure 2 shows the deviation of the present and the available data [5–11] from the correlation which was reported in the Thermophysical Property Tables of Refrigerants (CCl_2F_2; R 12) published by the Japanese Association of Refrigeration. The present data agree well with those of Michels *et al.* [7], Watanabe *et al.* [9], and Oguchi *et al.* [11]. As for $CBrF_3$, the comparison showed that the present data had no significant departure from the available data. Experimental uncertainties of the temperature and pressure were ±10 mK and ±3 kPa, respectively.

Table I. Experimental Results for Vapor Pressures of Pure Components

Temperature (K)	Vapor pressure (MPa)
Pure CCl_2F_2	
280.580	0.391
289.346	0.510
298.335	0.655
304.429	0.771
308.159	0.848
318.149	1.083
325.101	1.274
328.146	1.365
Pure $CBrF_3$	
287.863	1.253
294.147	1.465
299.256	1.657
304.404	1.869
314.749	2.352
325.151	2.928
330.281	3.250
335.688	3.618

3.2. Dew and Bubble Points

The dew- and bubble-point measurements of the $CCl_2F_2 + CBrF_3$ system were conducted for four different compositions of 0, 21.35, 44.82, and 70.24 mol% $CBrF_3$ in the range of temperatures from 299 to 384 K, pressures up to 4.2 MPa, and densities from 89 to 1228 $kg \cdot m^{-3}$. The results are given in Table II and illustrated on the P–T plane in Fig. 3 and on the T–ρ plane in Fig. 4. The density ρ is given in $kg \cdot m^{-3}$. The data for the densities 684.5 $kg \cdot m^{-3}$ of pure CCl_2F_2, 714.6 and 534.6 $kg \cdot m^{-3}$ of 21.35 mol% $CBrF_3$, 600.4 $kg \cdot m^{-3}$ of 44.82 mol% $CBrF_3$, and 679.1 and 652.1 $kg \cdot m^{-3}$ of 70.24 mol% $CBrF_3$ were measured with strong critical opalescence.

In comparing with the above-mentioned vapor pressure measurement, the temperature difference between the reappearance and the disappearance of the meniscus and the corresponding pressure change contribute to increase the uncertainties of the dew- and bubble-point temperature and pressure, which have been estimated not to exceed ±40 mK and ±5 kPa. The uncertainties of the density and the composition determinations were estimated to be not greater than ±1 and ±0.2%, respectively.

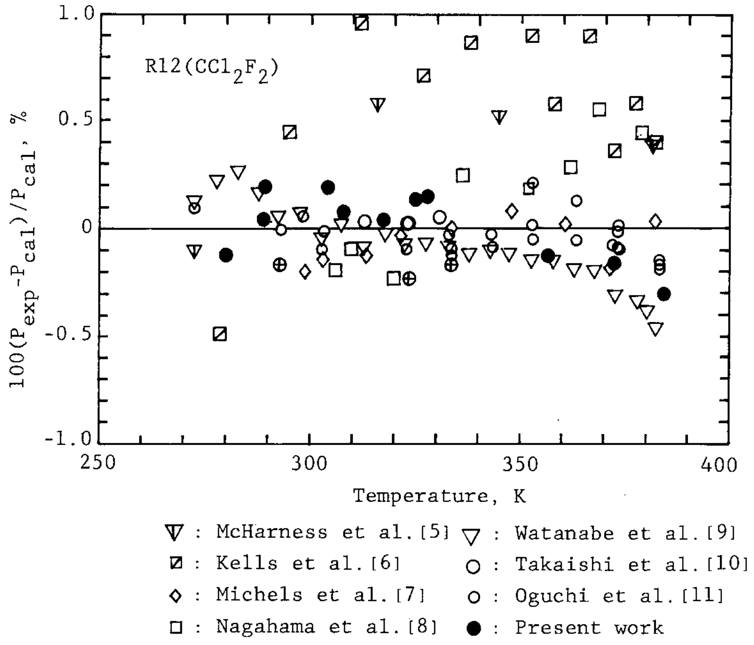


Fig. 2. Deviation of vapor pressure data for CCl_2F_2 from the correlation [12].

4. DISCUSSION

In Figs. 3 and 4, the dashed line denotes the critical locus estimated by the method of Chueh and Prausnitz [13]. It is found that the critical locus is a convex curve on the *P–T* plane and passes through the experimental data which showed critical opalescence.

The semiempirical Saove–Redlich–Kwong (SRK) equation of state was applied to calculate the dew- and bubble-point pressures. The two constants of the SRK equation of state for the mixture, a_m and b_m, were determined from the conventional mixing rules as follows:

$$a_m = \sum_i \sum_j x_i x_j (1 - k_{ij})(a_{ii} a_{jj})^{\frac{1}{2}} \tag{1}$$

$$b_m = \sum_i x_i b_{ii} \tag{2}$$

where x denotes the mole fraction and k_{ij} the so-called binary interaction parameter [14]. According to Soave's correlation, the pure-component

Table II. Experimental Results for Dew and Bubble Points of the $CCl_2F_2 + CBrF_3$ System[a]

Composition of $CBrF_3$					
mol%	wt%	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	
0	0	372.76	3.311	915.3	B
		384.37	4.070	684.5	B
		357.11	2.475	160.8	D
21.35	25.06	330.05	1.782	1228	B
		364.36	3.415	955.5	B
		368.17	3.660	917.4	B
		375.85	4.166	714.6	B
		376.51	4.173	534.6	D
		374.23	3.970	400.1	D
		367.92	3.517	299.5	D
		358.52	2.944	224.2	D
		347.70	2.375	167.8	D
		335.43	1.848	125.6	D
		322.79	1.397	94.0	D
44.82	50.01	350.09	3.186	1073	B
		365.24	4.153	802.4	B
		366.75	4.196	600.4	D
		366.21	4.073	449.2	D
		361.47	3.662	336.2	D
		353.46	3.101	251.7	D
		342.83	2.507	188.4	D
		331.40	1.972	141.0	D
		318.60	1.490	105.6	D
		307.15	1.134	79.1	D
70.24	74.40	339.28	3.154	1166	B
		352.16	3.966	907.6	B
		353.35	4.055	871.6	B
		354.95	4.129	679.1	D
		354.95	4.121	652.1	D
		354.84	4.057	508.1	D
		354.40	4.009	488.0	D
		350.30	3.684	380.3	D
		349.84	3.620	365.2	D
		342.88	3.163	284.7	D
		333.12	2.591	213.1	D
		322.28	2.047	159.5	D
		310.06	1.551	119.4	D
		299.09	1.184	89.4	D

[a] B, bubble point; D, dew point.

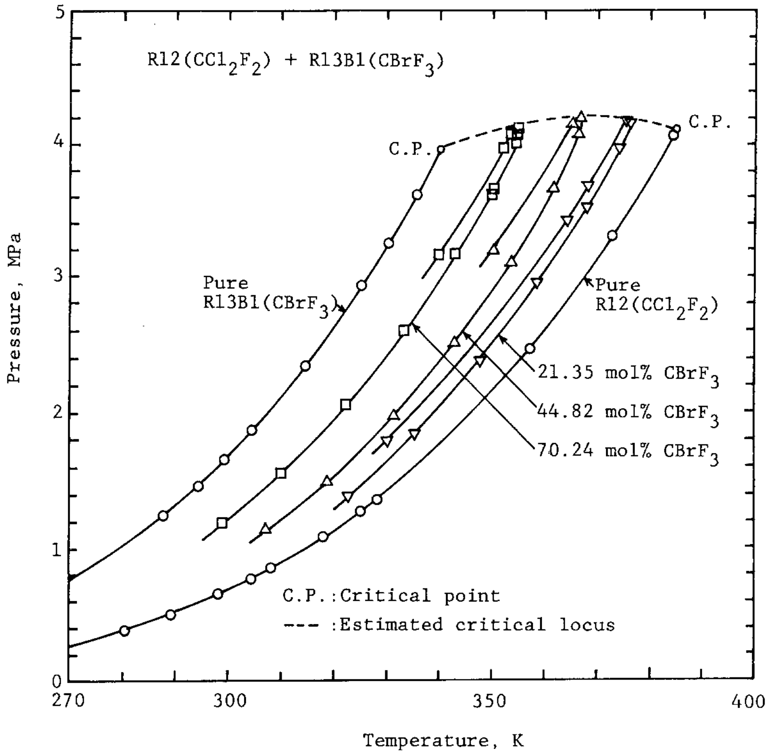


Fig. 3. Experimental results of dew and bubble points for the $CCl_2F_2 + CBrF_3$ system on the pressure–temperature plane.

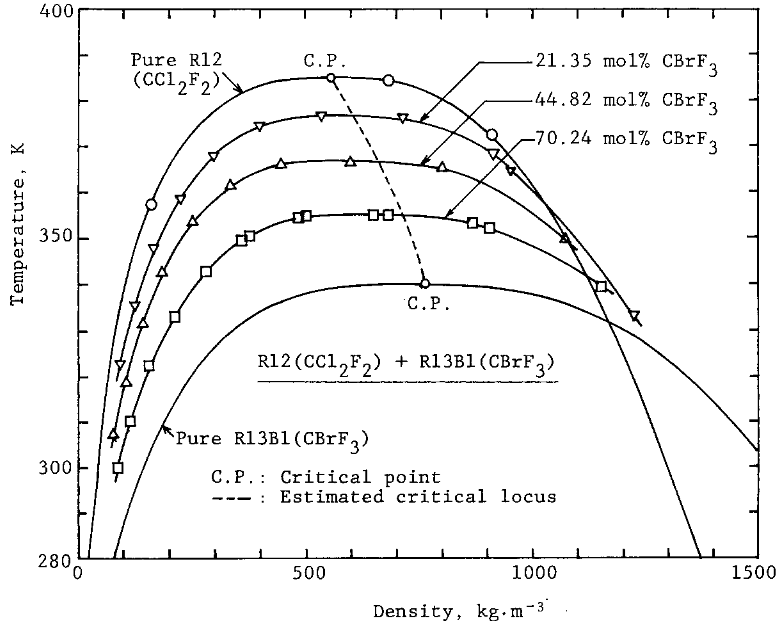


Fig. 4. Experimental results of dew and bubble points for the $CCl_2F_2 + CBrF_3$ system on the temperature–density plane.

Table III. Parameters of Pure Components

Component	CCl_2F_2	$CBrF_3$
Refrigerant number	R 12	R 13B1
Molecular weight	120.914	148.910
Boiling point at 1 atm (K)	243.358	215.29
Critical temperature (K)	384.95	340.08
Critical pressure (MPa)	4.125	3.956
Critical density ($kg \cdot m^{-3}$)	558	764
Acentric factor	0.179	0.173

constants, a_{ii}, a_{jj}, and b_{ii}, were calculated from the critical temperature and pressure [12, 15, 16] and the acentric factor, which are given in Table III. The calculated dew-point pressures deviated by 2.2% on average from 25 measured pressures when k_{ij} in Eq. (1) was optimized as −0.010. The deviations between the calculated and the measured bubble-point pressures exceed 10%. A typical P–x diagram at 323.15 K for the $CCl_2F_2 + CBrF_3$

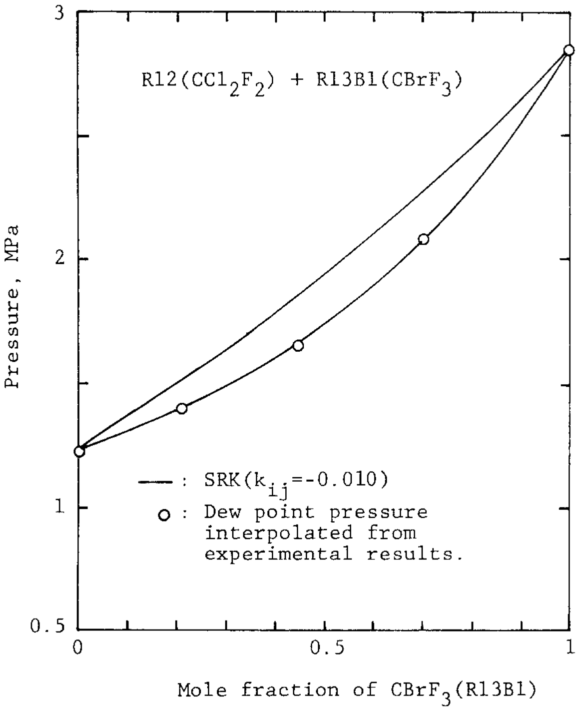


Fig. 5. Pressure–composition dew-point curve of the $CCl_2F_2 + CBrF_3$ system at 323.15 K.

system according to the SRK equation of state ($k_{ij} = -0.010$) is shown in Fig. 5. The system $CCl_2F_2 + CBrF_3$ shows a negative deviation from Raoult's law.

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