ρ_i density of pure component i
$\ln \eta^E$ excess logarithmic viscosity

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Bubble Point Pressures for Binary Mixtures of Bromotrifluoromethane (R13B1) and Chloropentafluoroethane (R115) with Chlorodifluoromethane (R22)

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The bubble point pressures for two binary mixtures of bromotrifluoromethane (R13B1) and chloropentafluoroethane (R115) with chlorodifluoromethane (R22) were measured by a new apparatus based on a static method employing a pressure vessel of 46-cm^3 volume. The results for various compositions covering the range of temperatures from 298.15 K to near their critical values were obtained. The uncertainty of the present data was estimated to be no greater than ±0.3%. The bubble point pressures for pure substances and an azeotropic mixture (R502) were correlated by the Wagner equation, and those for refrigerant mixtures were also correlated by the Wagner equation, based on the corresponding states principle.

Introduction

The binary mixtures of fluorocarbon refrigerants have been noted as new working fluids of heat pump and air conditioning units for the purpose of the effective application of thermal energy. For refrigerant mixtures, the direct measurement of the thermophysical properties, especially those of the equilibrium properties near the critical region, is difficult and has therefore seldom been investigated systematically.

In this work, we constructed a new apparatus based on a static method, which is able to measure the bubble point pressure of binary mixtures of fluorocarbon refrigerants over a wide range of temperature, and we present new experimental data for two binary systems: bromotrifluoromethane (R13B1) and chloropentafluoroethane (R115) with chlorodifluoromethane (R22), covering from 298.15 K to the neighborhood of the critical temperature.

The experimental results for three pure substances and an azeotropic mixture (R502) were successfully correlated by the Wagner equation, and those of two binary mixtures were also correlated by the Wagner equation using the corresponding states principle.

Table I. Melting Points T_f (*1*), Boiling Points T_b (*1*), Dipole Moments μ (*8*), Critical Temperatures T_c (*2*), Critical Pressures P_c (*2*), and Critical Densities ρ_c (*2*) of Refrigerants

refrigerant	T_f/K	T_b/K	$\mu/10^{30}$ Cm	T_c/K	P_c/MPa	ρ_c/(kg·m^{-3})
R22 ($CHClF_2$)	113	232.4	4.74	369.2	4.98	525
R13B1 ($CBrF_3$)	105	215.4	2.17	340.2	3.96	745
R115 ($CClF_2CF_3$)	167	235.2	1.73	353.2	3.12	596
R502 (48.8 wt % R22 + 51.2 wt % R115)	113	227.6		355.4	4.07	559

Experimental Section

Materials. Three refrigerants, chlorodifluoromethane, $CHClF_2$ (R22), bromotrifluoromethane, $CBrF_3$ (R13B1), and chloropentafluoroethane, C_2ClF_5 (R115), were supplied from the Daikin Kogyo Co., Ltd., as special research grade materials, and their purities were reported as being more than 99.9 wt %. The physical properties of pure refrigerants are listed in Table I, along with those of R502, which is an azeotropic mixture of R115 and R22 (*1*, *2*, *8*).

Apparatus. There are basically two types of bubble point pressure measurements, that is, the dynamic method at constant pressure and the static one at constant temperature. In this work, a new apparatus of the static method was constructed, and the schematic diagram is shown in Figure 1. The apparatus consists primarily of a sample cell (1), a thermostated oil bath (2), a thermostated air bath (3), a U-tube-type detector containing mercury (4), an oil-operated dead-weight gage (5), an oil pump (6), a pressure gage (7), a vacuum pump (8), and pipe lines.

Bubble Point Pressure Measurements. The sample cell was made of a low-density aluminum alloy (Cu, 3.5–4.5%; Si, less than 0.8%; Fe, less than 1.0%; Mn, 0.4–1.0%; Mg, 0.2–0.8%; Al, the rest) (*9*), and its volume was about 46 cm^3. Each component of the desired binary system was individually introduced into the sample cell, which was previously evacuated, by slow distillation until it was almost full and a small amount of vapor phase remained. The composition of the refrigerant mixtures was determined by measuring the weight of each component of the mixtures by use of a precision direct-reading

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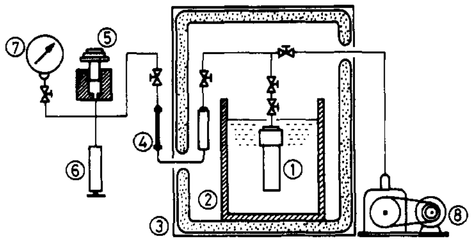

Figure 1. Schematic diagram of the experimental apparatus: (1) sample cell, (2) thermostated oil bath, (3) thermostated air bath, (4) U-tube detector, (5) dead-weight gage, (6) oil pump, (7) Bourdon gage, (8) vacuum pump.

Table II. Experimental Bubble Point Pressures P for the R13B1-R22 System at Weight Percent w (Mole Fraction x) of R22 and Temperatures T

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
w = 0 (x = 0) (R13B1)					
298.15	1.625	318.15	2.536	336.15	3.640
303.15	1.830	323.15	2.811	337.15	3.705
308.15	2.042	328.15	3.116	338.15	3.762
313.15	2.280	333.15	3.427		
w = 25.0 (x = 0.365)					
298.15	1.537	344.65	4.056	345.90	4.162
303.15	1.740	344.81	4.068	346.00	4.174
308.15	1.946	344.90	4.077	346.10	4.184
313.15	2.172	345.00	4.085	346.25	4.195
318.15	2.400	345.10	4.094	346.35	4.203
323.15	2.675	345.20	4.106	346.45	4.211
328.15	2.949	345.31	4.114	346.55	4.224
333.15	3.240	345.40	4.122	346.70	4.241
338.15	3.591	345.50	4.130	346.80	4.252
343.15	3.929	345.60	4.138	346.90	4.263
344.16	4.016	345.70	4.147		
w = 50.0 (x = 0.633)					
298.15	1.386	353.15	4.353	355.95	4.628
303.15	1.573	354.15	4.463	356.05	4.638
308.15	1.754	354.65	4.506	356.15	4.647
313.15	1.977	354.94	4.533	356.25	4.659
318.15	2.180	355.15	4.555	356.40	4.675
323.15	2.430	355.25	4.567	356.50	4.686
328.15	2.692	355.36	4.573	356.60	4.696
333.15	2.976	355.51	4.585	356.70	4.706
338.15	3.283	355.60	4.596	356.80	4.717
343.15	3.604	355.75	4.609	356.90	4.725
348.15	3.975	355.85	4.619		
w = 75.0 (x = 0.838)					
298.15	1.219	323.15	2.189	348.15	3.635
303.15	1.388	328.15	2.414	353.15	3.990
308.15	1.566	333.15	2.688	358.15	4.365
313.15	1.758	338.15	2.941	363.15	4.757
318.15	1.949	343.15	3.286	364.15	4.857
w = 100 (x = 1) (R22)					
298.15	1.044	333.15	2.426	366.15	4.689
303.15	1.197	338.15	2.700	367.15	4.782
308.15	1.365	343.15	2.992	368.15	4.873
313.15	1.541	348.15	3.298	368.65	4.922
318.15	1.730	353.15	3.662	368.85	4.941
323.15	1.944	358.15	4.031	369.05	4.960
328.15	2.172	363.15	4.435	369.15	4.970

Table III. Experimental Bubble Point Pressures P for the R115-R22 System at Weight Percent w (Mole Fraction x) of R22 and Temperatures T

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
w = 0 (x = 0) (R115)					
298.15	0.9137	318.15	1.492	343.15	2.547
303.15	1.044	323.15	1.669	348.15	2.803
308.15	1.180	328.15	1.853	353.15	3.103
313.15	1.324	333.15	2.065		
w = 25.0 (x = 0.373)					
298.15	1.124	323.15	2.002	348.15	3.342
303.15	1.262	328.15	2.226	351.15	3.536
308.15	1.439	333.15	2.473	353.15	3.681
313.15	1.607	338.15	2.734	354.15	3.744
318.15	1.801	343.15	3.021		
w = 48.8 (x = 0.630) (R502)					
298.15	1.153	338.15	2.885	354.75	4.028
303.15	1.312	343.15	3.191	354.95	4.046
308.15	1.486	348.15	3.527	355.05	4.057
313.15	1.671	353.15	3.894	355.15	4.067
318.15	1.879	353.65	3.932	355.20	4.070
323.15	2.100	354.15	3.972	355.25	4.075
328.15	2.339	354.55	4.004	355.30	4.078
333.15	2.599				
w = 75.0 (x = 0.843)					
298.15	1.120	353.15	3.830	360.00	4.375
303.15	1.275	358.15	4.213	360.10	4.384
308.15	1.441	358.66	4.253	360.20	4.397
313.15	1.634	359.15	4.296	363.15	4.601
318.15	1.843	359.31	4.309	364.15	4.702
323.15	2.056	359.41	4.317	365.15	4.812
328.15	2.292	359.61	4.331	365.35	4.838
333.15	2.557	359.70	4.342	365.55	4.856
338.15	2.838	359.80	4.352	365.74	4.873
343.15	3.143	359.90	4.360	365.95	4.893
348.15	3.475				

balance accurate to 0.1 mg (maximum of 1 kg). A Teflon chip (about 10 × 20 mm) in the sample cell provided good agitation of the refrigerant mixtures with shaking of the cell by hand before the cell was connected to the piping system. The sample cell was then placed in the oil bath, which was kept at a given temperature within ±10 mK. The oil bath was covered with the air bath, lined with an insulating material, glass wool, to diminish heat loss. The temperature of the sample was regarded as that of the oil in the bath, as ample time (4–5 h) was allowed for the establishment of vapor–liquid equilibrium. The bubble point pressure measurement was repeated to ascertain that the measured value did not change. The temperature was measured by a thermistor thermometer calibrated against the reference thermometer, provided with a calibration certificate by the National Research Laboratory of Metrology of Japan. The precision of the temperature measurement was ±10 mK.

The high-pressure tube used for the piping system (1-mm inside diameter) was filled with the vapor of the sample, after evacuation by a vacuum pump. However, the composition change of the refrigerant mixtures was considered to be small, because the inside volume of the tubing was very small compared with that of the sample cell; the resulting error of weight fraction in the liquid phase was less than 0.001. The bubble point pressure of the sample was measured by the dead-weight gage within a precision of ±1 kPa. The U-tube-type detector for balancing pressure was set up between the sample cell and the dead-weight gage to separate oil and vapor. One side of the U-tube was made of Pyrex-glass capillary, and the pressure balance was detected by observing the position of the mercury level by eye.

The bubble point pressure measurements for binary mixtures having compositions for R22 of w = 0, 25, 50, 75, and 100 wt %, corresponding to mole fractions x = 0, 0.365, 0.633, 0.838, and 1 in the R13B1–R22 system, and of w = 0, 25, 48.8 (R502), and 75, corresponding to x = 0, 0.373, 0.630 (R502), and 0.843 in the R115–R22 system, were made in the range of temperatures from 298 to 370 K.

Results and Discussion

The experimental bubble point pressures P for binary mixtures of R13B1–R22 and R115–R22 at several weight fractions w (mole fractions x) and temperatures T are summarized in Tables II and III. In this work, the measurements were carried out at narrow temperature intervals, especially near the

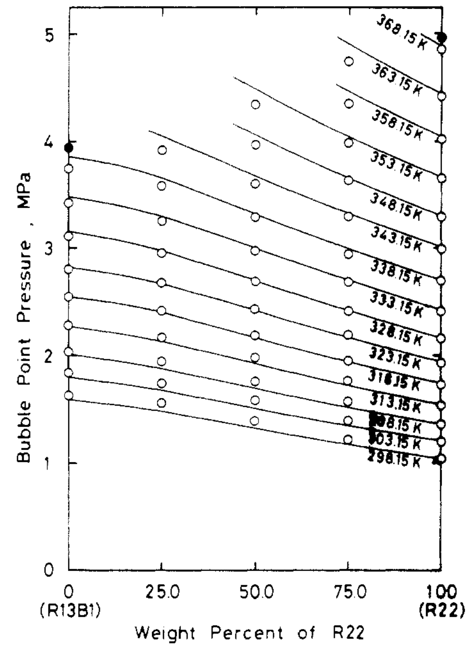

Figure 2. Vapor pressure of the R13B1-R22 system as a function of composition: (○) this work, (●) critical point; (—) calculated result.

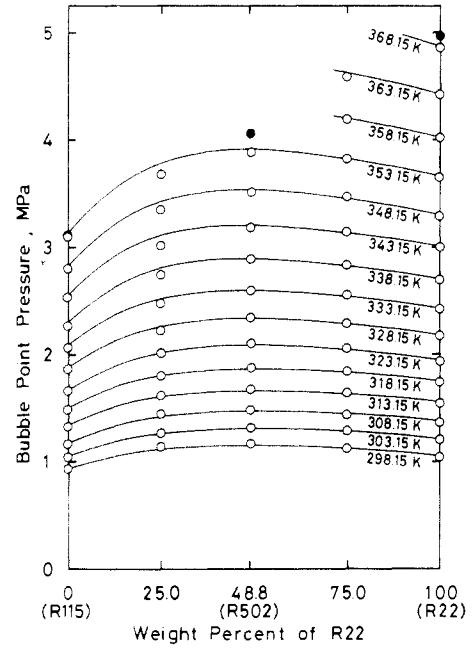

Figure 3. Vapor pressure of the R115-R22 system as a function of composition: (○) this work, (●) critical point; (—) calculated result.

critical region, where the bubble point pressure depends largely on temperature for each composition. *P* represents the smooth change against temperature and composition. For pure fluorocarbon refrigerants, the *P* values have so far been reported in many investigations (*1–5*). The present results for R22 and R502 agree with those reported in refs 2–4, with average deviations of 0.3% for R22 and 0.2% for R502 throughout the entire temperature range. The experimental data for R13B1 and R115 in the vicinity of the critical temperature were lower by a maximum deviation of 1.4% for R13B1 and 1.6% for R115 compared with literature values (*1*, *2*, *5*). The *P* values obtained in this study were reproducible within 0.15% for each composition on repeated runs. From the facts, taking into account the observed errors of temperature and pressure, the precision of the measurements of the bubble point pressure presented here was estimated to be no greater than ±0.3%.

Table IV. Constants in the Wagner Equation (Equations 1, 3, and 5) and Relative Average Deviations δ_{av} between Calculated (P_{cal}) and Experimental (P) Bubble Point Pressures for Pure Refrigerants and the Azeotropic Mixture R502

	n	*A*	*B*	*C*	*D*	δ_{av}[a]
R22	21	−6.998 86	1.222 89	−2.353 15	−3.243 45	0.20
R13B1	11	−6.757 73	1.203 24	−1.997 31	−3.845 12	0.47
R115	12	−7.431 10	2.412 37	−6.250 52	−4.848 82	0.31
R502	22	−7.466 37	2.640 18	−5.968 21	9.998 79	0.46

[a] $\delta_{av} = 100\sum[|P - P_{cal}|/P_{cal}]/n$, where *n* is the number of data points.

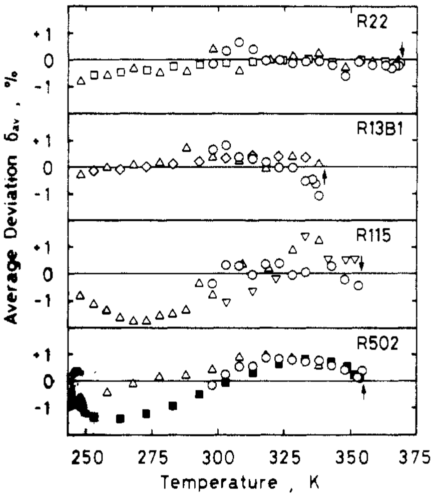

Figure 4. Average deviation in vapor pressure correlation by the Wagner equation: (↓ or ↑) critical temperature; (○) this work, (◇) ref 1, (△) ref 2, (□) ref 3, (■) ref 4, (▽) ref 5.

The experimental bubble point pressures of the mixture for the R13B1–R22 and R115–R22 systems are plotted against the composition in Figures 2 and 3, respectively. As can be seen in the figures, the *P* values for the R13B1–R22 system decrease with increasing weight percent of R22, while those for the R115–R22 system show the convex curves having a maximum at the azeotropic composition.

A successful equation for correlating bubble point pressures of pure liquids was presented by Wagner (*6*). The Wagner equation is expressed as follows:

$$\ln\left(\frac{P}{P_c}\right) = \frac{1}{1-\tau}(A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6) \qquad (1)$$

where

$$\tau = 1 - \frac{T}{T_c} \qquad (2)$$

The constants *A*, *B*, *C*, and *D* for pure and azeotropic refrigerants were determined by fitting the calculated values from eq 1 to both the present data and the literature data (*1–5*) in the temperature range from 250 to 370 K, and are given in Table IV. The critical values required in this calculation are listed in Table I. The deviations of the present and literature data from eq 1 for four substances are plotted in Figure 4, and the average deviation δ_{av} between the present data and the calculated values is shown in Table IV. It was found that eq 1 gave the best reproducibility to the present and literature data for R22 (*2*, *3*) in this temperature range. At all events, the bubble point pressures of the three pure substances and one azeotropic mixture could be correlated with eq 1, with a maximum deviation of 1.8%.

The bubble point pressures of the refrigerant mixtures were correlated by the Wagner equation based on the method of the corresponding states principle because mixing rules for the

Table V. Molecular Shape Factors θ_i and ϕ_i, Binary Interaction Parameters k_{12} (Equations 3-8), and Relative Average Deviations between Calculated (P_{cal}) and Experimental (P) Bubble Point Pressures δ_{av} for Refrigerant Mixtures, as a Function of Weight Percent w of R22

	θ_i	ϕ_i	k_{12}	w	n	δ_{av}[a]
R13B1-R22	1.0	1.0189	-0.177	0.0	11	1.5
				25.0	32	2.8
				50.0	32	2.4
				75.0	15	2.0
R115-R22	1.0	0.9923	-0.282	0.0	11	0.23
				25.0	14	1.9
				48.8	22	0.49
				75.0	31	0.63

[a] See footnote to Table IV.

constants A, B, C, and D are not known. It is necessary to introduce molecular shape factors, θ and ϕ, to the system containing normal fluids, which deviate from the corresponding states principle in two variables (*7*). So, $\theta_i T_{ci}$ and $\phi_i P_{ci}$ (i = 1,2) were used instead of critical constants, T_{ci} and P_{ci}, where subscript 1 is R13B1 and 2 is R115. In this study, R22 is chosen as the reference substance and denoted by subscript 0. The bubble point pressures of R13B1 and R115 were correlated again by the following equations by using the constants A_0, B_0, C_0, and D_0 of the reference substance R22.

$$\ln\left(\frac{P_i}{\phi_i P_{ci}}\right) = \frac{1}{1-\tau_i}(A_0\tau_i + B_0\tau_i^{1.5} + C_0\tau_i^3 + D_0\tau_i^6) \quad (3)$$

where

$$\tau_i = 1 - \frac{T}{\theta_i T_{ci}} \quad (4)$$

The values of θ_i and ϕ_i were determined by fitting calculated P to measured P_i of R13B1 and R115. The molecular shape factors of R13B1 and R115 obtained are found to be constant in this temperature range, and given in Table V. The calculated bubble point pressures from eq 3 by the use of θ_i and ϕ_i, listed in Table V, reproduced the measured values with the average deviations of 1.7% and 2.2% for pure R13B1 and R115, respectively.

The bubble point pressures of the refrigerant mixtures P_m were represented by the following equations:

$$\ln\left(\frac{P_m}{P_{cm}}\right) = \frac{1}{1-\tau_m}(A_0\tau_m + B_0\tau_m^{1.5} + C_0\tau_m^3 + D_0\tau_m^6) \quad (5)$$

where

$$\tau_m = 1 - \frac{T}{T_{cm}} \quad (6)$$

The pseudocritical constants for the mixtures P_{cm} and T_{cm} in eqs 5 and 6 were calculated from the following empirical mixing rules containing the binary interaction parameter k_{12}

$$T_{cm} = x_0 T_{c0} + x_i(\theta_i T_{ci}) \quad (7)$$

$$P_{cm} = x_0^2 P_{c0} + 2x_0 x_i(1-k_{12})[P_{c0}(\phi_i P_{ci})]^{1/2} + x_i^2(\phi_i P_{ci}) \quad (8)$$

where x is the mole fraction. k_{12} was also regarded as a fitting parameter. k_{12} values obtained in this study are listed in Table V, together with the average deviation in each system. The calculated bubble point pressures P_m from eq 5 with eqs 6-8 are denoted by solid lines in Figures 2 and 3. As shown in the figures, the calculated values agreed with the experimental ones within the maximum deviations of 4.7% and 2.2% for the R13B1-R22 and R115-R22 system, respectively. As is evident from the result mentioned above, it may be concluded that the estimation of the bubble point pressures of fluorocarbon refrigerant mixtures is possible by the Wagner equation, based on the corresponding states principle using molecular shape factors.

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