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Bubble Point Pressures for Chlorodifluoromethane + 1,2-Dichloro-1,1,2,2-tetrafluoroethane, Bromotrifluoromethane + 1,2-Dichloro-1,1,2,2-tetrafluoroethane, and Bromotrifluoromethane + Chloropentafluoroethane

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The bubble point pressures for chlorodifluoromethane (R22) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), bromotrifluoromethane (R13B1) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), and bromotrifluoromethane (R13B1) + chloropentafluoroethane (R115) were measured by a static method. Measurements were made at various compositions at temperatures from 298.15 K to near their critical temperature. The uncertainty of the pressures was estimated to be no greater than ±0.3%. The bubble point pressures for pure substances were correlated by the Wagner equation, and those for the mixtures were also correlated by the Wagner equation, using a corresponding states principle.

Introduction

The advantage of using binary mixtures of fluorocarbon refrigerants has been discussed from the point of view that thermal energy should be used effectively (*1*). The equilibrium properties near the critical region for refrigerant mixtures should be known accurately for system design and reliable assessment of the cycle performance. However, their direct measurement is difficult and has therefore seldom been investigated systematically.

The bubble point pressures for two binary mixtures of bromotrifluoromethane (R13B1) and chloropentafluoroethane (R115) with chlorodifluoromethane (R22) were measured and correlated in a previous paper (*2*). In this work, the bubble point pressures for chlorodifluoromethane (R22) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), bromotrifluoromethane (R13B1) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), and bromotrifluoromethane (R13B1) + chloropentafluoroethane (R115) are reported from 298.15 K to the neighborhood of the critical temperature.

The present results for the pure substance were successfully correlated by the Wagner equation, and those of three binary mixtures were also correlated by the Wagner equation using a corresponding states principle, by which the previous data for R13B1 + R22 and R115 + R22 were correlated with good agreement.

Experimental Section

Materials. Four refrigerants, chlorodifluoromethane (R22), bromotrifluoromethane (R13B1), 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), and chloropentafluoroethane (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 %. Their critical pressures and temperatures are listed in Table I.

Table I. Critical Properties of Refrigerants (*3*)

refrigerant	T_c/K	P_c/MPa
R22 ($CHClF_2$)	369.2	4.98
R13B1 ($CBrF_3$)	340.2	3.96
R115 (C_2ClF_5)	353.2	3.12
R114 ($C_2Cl_2F_4$)	418.9	3.27

Apparatus. The static apparatus described previously (*2*) was used. The procedures for the bubble point pressure measurements were described in the previous paper. The precision of the temperature measurement was ±10 mK, and the bubble point pressure was measured within a precision of ±1 kPa. The measurement error of mass fraction for the liquid sample was less than 0.001. The bubble point pressures obtained in this study were reproducible within ±0.15% for each composition on repeated runs. The precision of the measurements of bubble point pressure presented here was estimated to be no greater than ±0.3%.

Results and Discussion

The experimental bubble point pressures P for three binary mixtures, R22 + R114, R13B1 + R114, and R13B1 + R115, at several mass fractions w (mole fractions x) and temperatures T are summarized in Tables II–IV. In this work, the measurements were carried out at narrow temperature intervals, especially near the critical region, where the bubble point pressure depends largely on temperature for each composition. For pure fluorocarbon refrigerants, the bubble point pressures have been reported in many investigations (*3, 4*). As shown in the previous paper (*2*), the results on the bubble point pressure for the pure refrigerants of R22, R13B1, and R115 agreed with those reported in refs 1 and 3–7. The results for R22 agreed with the literature values with average deviations of 0.3%, and those for R13B1 and R115 in the vicinity of the critical temperature were lower by maximum deviations of 1.4% and 1.6%, respectively. Similarly, the present results for pure R114 agree with those reported in ref 3. The results agree by a maximum deviation of 2.3% compared with literature values (*3*).

The experimental bubble point pressures of the three binary mixtures R22 + R114, R13B1 + R114, and R13B1 + R115 are plotted against composition in Figures 1–3, respectively. The bubble point pressures for R22 + R114 and R13B1 + R114 decrease with increasing mass percent of R114, and those for R13B1 + R115 decrease with increasing mass percent of R115.

In the present study, the Wagner equation (8) is used to correlate the bubble point pressures (i.e., vapor pressures for

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Table II. Experimental Bubble Point Pressures P for R22 + R114 at Mass Percent w (Mole Fraction x) of R22 and Temperatures T

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$w = 0$ ($x = 0$) (R114)					
298.15	0.219	328.15	0.504	358.15	1.038
303.15	0.255	333.15	0.572	363.15	1.154
308.15	0.294	338.15	0.647	368.15	1.257
313.15	0.343	343.15	0.736		
318.15	0.393	348.15	0.830		
323.15	0.445	353.15	0.930		
$w = 25.0$ ($x = 0.397$)					
298.15	0.597	328.15	1.187	358.15	2.076
303.15	0.678	333.15	1.318	363.15	2.237
308.15	0.764	338.15	1.453	368.15	2.440
313.15	0.863	343.15	1.597		
318.15	0.959	348.15	1.773		
323.15	1.070	353.15	1.897		
$w = 50.0$ ($x = 0.664$)					
298.15	0.802	323.15	1.438	348.15	2.303
303.15	0.912	328.15	1.602	353.15	2.513
308.15	1.028	333.15	1.758	358.15	2.708
313.15	1.175	338.15	1.922	363.15	2.941
318.15	1.298	343.15	2.086		
$w = 75.0$ ($x = 0.856$)					
298.15	0.931	328.15	1.874	358.15	3.436
303.15	1.067	333.15	2.063	363.15	3.768
308.15	1.185	338.15	2.287		
313.15	1.338	343.15	2.526		
318.15	1.490	348.15	2.828		
323.15	1.691	353.15	3.130		

Table III. Experimental Bubble Point Pressures P for R13B1 + R114 at Mass Percent w (Mole Fraction x) of R13B1 and Temperatures T

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$w = 25.0$ ($x = 0.277$)					
298.15	0.545	328.15	1.054	358.15	1.805
303.15	0.616	333.15	1.164	363.15	1.977
308.15	0.691	338.15	1.283	368.15	2.117
313.15	0.771	343.15	1.405		
318.15	0.861	348.15	1.535		
323.15	0.955	353.15	1.663		
$w = 50.0$ ($x = 0.534$)					
298.15	0.891	323.15	1.495	348.15	2.250
303.15	0.998	328.15	1.635	353.15	2.400
308.15	1.108	333.15	1.796	358.15	2.548
313.15	1.228	338.15	1.943	363.15	2.725
318.15	1.358	343.15	2.090		
$w = 75.0$ ($x = 0.775$)					
298.15	1.246	313.15	1.713	328.15	2.240
303.15	1.391	318.15	1.877	333.15	2.443
308.15	1.546	323.15	2.053	338.15	2.632

a pure substance) of pure R114. 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

$$\tau = 1 - T/T_c \qquad (2)$$

The constants A–D for R114 were determined by fitting the calculated values from eq 1 to the present data in the temperature range from 298.15 to 368.15 K, and are given in Table V. The critical values required in this calculation are listed in Table I. The deviations of the present data and literature data (*3*) from eq 1 for R114 are plotted in Figure 4, and the average deviation between the present data and the calculated values is shown in Table V. The bubble point pressures of R114 could be correlated with eq 1, with a maximum deviation of 1.9%.

Table IV. Experimental Bubble Point Pressures P for R13B1 + R115 at Mass Percent w (Mole Fraction x) of R13B1 and Temperatures T

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$w = 25.0$ ($x = 0.257$)					
298.15	1.108	323.15	1.909	348.15	3.134
303.15	1.249	328.15	2.123	349.15	3.210
308.15	1.401	333.15	2.336	350.15	3.275
313.15	1.561	338.15	2.571		
318.15	1.727	343.15	2.844		
$w = 50.0$ ($x = 0.509$)					
298.15	1.287	328.15	2.415	349.15	3.635
303.15	1.447	333.15	2.658	349.65	3.673
308.15	1.616	338.15	2.939	350.15	3.708
313.15	1.802	343.15	3.239	350.65	3.745
318.15	1.986	348.15	3.566	351.15	3.776
323.15	2.189	348.65	3.599		
$w = 75.0$ ($x = 0.757$)					
298.15	1.442	323.15	2.481	344.05	3.748
303.15	1.631	328.15	2.734	345.15	3.812
308.15	1.813	333.15	3.026	345.65	3.853
313.15	2.028	338.15	3.306		
318.15	2.241	343.15	3.682		

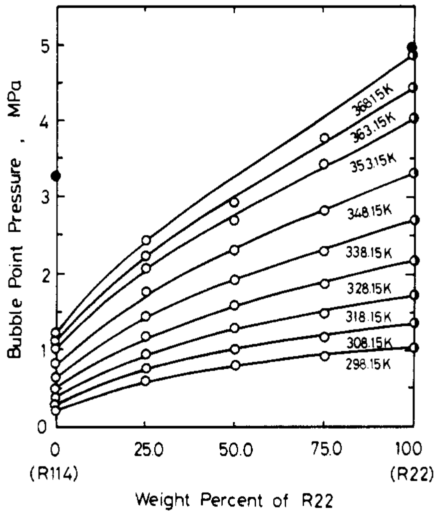

Figure 1. Bubble point pressures for R22 + R114 as a function of composition: (○) this work, (◐) previous work, (●) critical point; (—) calculated result.

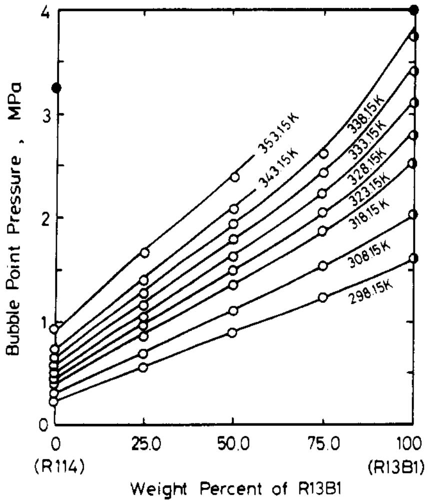

Figure 2. Bubble point pressures for R13B1 + R114 as a function of composition: (○) this work, (◐) previous work, (●) critical point; (—) calculated result.

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

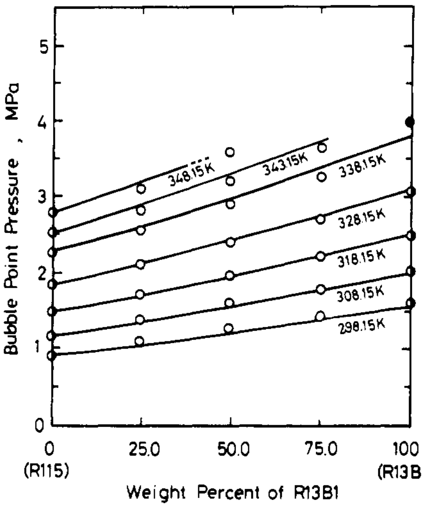

Figure 3. Bubble point pressures for R13B1 + R115 as a function of compositions: (○) this work, (◑) previous work, (●) critical point; (—) calculated result.

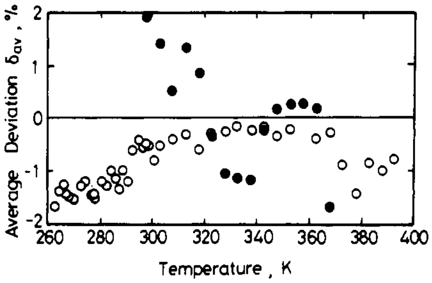

Figure 4. Average deviation in the bubble point pressure correlation for R114 by the Wagner equation; (●) this work, (○) ref 3.

Table V. Constants in the Wagner Equation (Equations 1 and 2) and Relative Average Deviation δ_{av} between Calculated (P_{calcd}) and Experimental (P) Bubble Point Pressures for Pure Refrigerants

	n	A	B	C	D	δ_{av}[a]
R114	15	−7.335 82	1.624 82	−3.062 34	−2.422 81	0.83
R22	21	−6.998 86	1.222 89	−2.353 15	−3.243 45	0.20

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

for the constants A–D are not known. It is necessary to introduce molecular shape factors, θ and ϕ, to the system containing normal fluids, which deviates from the corresponding states principle in two variables (*9*). So, θ_iT_{ci} and ϕ_iP_{ci} ($i = 1, 2$) were used instead of critical constants, T_{ci} and P_{ci}. In this study, as in the previous paper (*2*), R22 is chosen as the reference substance and denoted by subscript 0, whose constants A–D are presented in Table V. The bubble point pressures of R114 were correlated again by the following equation by using the constants A_0–D_0 of the reference substance R22:

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

where

$$\tau_i = 1 - T/\theta_iT_{ci} \quad (4)$$

The shape factors of R114 are found to be constant in this temperature range, and given in Table VI. The calculated bubble point pressures from eq 3 using the θ_i and ϕ_i values listed in Table VI reproduced the measured values with the average deviation of 0.88% for R114. The shape factors for R13B1 and R115 determined in the previous study (*2*) are also shown in Table VI. The bubble point pressures of refrigerant mixtures P_m were represented by the following equation:

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

where

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

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}:

$$T_{cm} = x_1\theta_1T_{c1} + x_2\theta_2T_{c2} \quad (7)$$

$$P_{cm} = x_1^2\phi_1P_{c1} + 2x_1x_2(1 - k_{12})[\phi_1P_{c1}\phi_2P_{c2}]^{1/2} + x_2^2\phi_2P_{c2} \quad (8)$$

x is the mole fraction, and subscripts 1 and 2 are components 1 and 2. For the expression of k_{12}, an asymmetric mixing rule, proposed by Adachi et al. (*10*), which depends on mole fraction was adopted as follows:

$$k_{12} = k_{12}^{(0)} + k_{12}^{(1)}(T - T_{12}^{(0)}) + m_{12}(x_1 - x_2) \quad (9)$$

where $k_{12}^{(0)}$, $k_{12}^{(1)}$, $T_{12}^{(0)}$, and m_{12} are adjustable parameters. These parameters obtained in this work are listed in Table VI, together with the average deviation in each system. The calculated bubble point pressures P_m from eq 5 with eqs 6–9 are denoted by solid lines in Figures 1–3. The calculated values agree with experiment within the maximum deviations of 3.1%, 3.4%, and 5.2% for R22 + R114, R13B1 + R114, and R13B1 + R115, respectively. However, for R13B1 + R115, the experimental bubble point pressures near the critical region could not be correlated with this method because the present mixing rule gives $T_{cm} < T$. From the result mentioned above, it is concluded that the estimation of the bubble point pressures of fluorocarbon refrigerant mixtures is possible by

Table VI. Molecular Shape Factors θ_i and ϕ_i, Binary Interaction Parameters $k_{12}^{(0)}$, $k_{12}^{(1)}$, m_{12}, and $T_{12}^{(0)}$, and Relative Average Deviations between Calculated (P_{calcd}) and Experimental (P) Bubble Point Pressures (δ_{av}) for Refrigerant Mixtures, as a Function of Mass Percent w of Component 1

mixture	component	θ_i	ϕ_i	$k_{12}^{(0)}$	$k_{12}^{(1)}$	m_{12}	$T_{12}^{(0)}$	w	n	δ_{av}[a]
R22 (1) + R114 (2)	1	1.0	1.0	0.539	0.007 84	0.237	462.1	0.0	15	0.88
								25.0	15	1.4
	2	1.0	0.9517					50.0	14	1.1
								75.0	14	1.5
R13B1 (1) + R114 (2)	1	1.0	1.1089	−2.024	0.0130	0.434	210.2	25.0	15	2.3
								50.0	14	1.4
	2	1.0	0.9517					75.0	9	0.74
R13B1 (1) + R115 (2)	1	1.0	1.1089	0.001 30	0	0	0	25.0	12	2.1
								50.0	10	2.5
	2	1.0	0.9923					75.0	10	2.0

[a] See footnote *a* in Table V.

the Wagner equation, based on the corresponding states principle using molecular shape factors.

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