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Bubble Pressures and Saturated Liquid Densities of R 22 + R 114 Mixtures in the Range 310 – 400 K

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The bubble pressures and saturated liquid densities of mixtures of R 22 and R 114 have been measured with a static and synthetic method with a variable-volume cell. The results for five different compositions (100, 75, 50, 25, and 0 mol% R 22) cover the temperature range from 310 to 400 K. The experimental data for both pure components are compared with literature data, showing the reliability of the present results. The system shows positive deviations from Raoult's law at temperatures below 340 K and the deviations increase with decreasing temperature. The 25 mol% R 22 mixture shows the maximum nonideality.

KEY WORDS: bubble pressure; R 114; R 22; refrigerants; refrigerant mixtures; saturated liquid density.

1. INTRODUCTION

The advantage of using mixtures of R 22 and R 114 for energy saving in refrigeration and heat pump systems is well known [1], and experimental data on the thermodynamic properties of this system have recently been reported by several institutions [2–5]. In this paper, we present bubble pressures and saturated liquid densities of this system including both pure components at 10 temperatures from 310 to 400 K. The measurements have been obtained with the static and synthetic method with a variable-volume cell composed of a metal bellows. The purity of the two components was 99.99 wt% R 22 (chlorodifluoromethane, $CHClF_2$) and 99.97 wt% R 114 (dichlorotetrafluoroethane) with an isomeric blend of 95% $CClF_2CClF_2$ + 5% CCl_2FCF_3.

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2. EXPERIMENTAL

The bubble pressures and saturated liquid densities have been determined by finding breaking points in the experimental isotherms for mixtures of fixed compositions in a pressure–density plane. The apparatus and experimental procedure have been described in detail in a previous publication [6]. The equilibrium cell was composed of a metal bellows made of stainless steel (AM350) and a pressure vessel made of 304 stainless steel. The sample of known mass and composition was filled in the bellows. The bellows has a length of 75 mm, a thickness of 0.15 mm, an outer diameter of 30 mm, and an effective cross-sectional area of 4.3 cm^2. The bellows hung vertically downward in the pressure vessel and traveled longitudinally upward to a maximum distance of 16 mm. The volume of the bellows at the reference position was about 27 cm^3. The pressure vessel was immersed in a circulating silicone-oil bath. The temperature of the pressure vessel was set at the desired value within ±3 mK and it was kept constant within ±3 mK during the measurements of a given isotherm. The temperature was measured with a 25-Ω platinum resistance thermometer (Chino Model R 800-2) calibrated with a precision of 2 mK on the IPTS-68. The thermometer was placed in a well drilled in the pressure vessel. After confirming that the sample was in thermodynamic equilibrium, the measured temperature of the pressure vessel was regarded to be the sample temperature. The uncertainty in the temperature measurements was estimated to be no greater than ±6 mK.

The bellows was compressed or expanded by applying or reducing the pressure of nitrogen gas in the pressure vessel surrounding the bellows. The

Table I. Experimental Results for the Bubble Pressure (MPa) of R 22 + R 114 Mixtures

	Mole fraction of R 22				
T(K)	1.000	0.750	0.500	0.250	0.000
310	1.4184	1.1628	0.9186	0.6343	0.3082
320	1.8052	1.4745	1.1559	0.8041	0.4102
330	2.2650	1.8510	1.4510	1.0055	0.5349
340	2.8065	2.2855	1.7697	1.2517	0.6849
350	3.4406	2.7552	2.1366	1.5386	0.8669
360	4.1821	3.3517	2.5503	1.8634	1.0810
370		3.9724	3.0324	2.1904	1.3319
380		4.6345	3.5476	2.5986	1.6225
390			4.1090	3.0055	1.9602
400				3.4986	2.3491

Table II. Experimental Results for the Saturated Liquid Density (kg · m^{-3}) of R 22 + R 114 Mixtures

T (K)	Mole fraction of R 22				
	1.000	0.750	0.500	0.250	0.000
310	1143.1	1226.0	1296.6	1358.8	1416.0
320	1097.6	1183.2	1258.6	1324.6	1382.4
330	1047.5	1137.9	1217.6	1287.2	1347.6
340	990.4	1087.2	1172.9	1246.4	1311.6
350	920.1	1025.5	1120.5	1201.7	1270.5
360	823.6	947.6	1065.4	1153.9	1228.4
370		869.1	1002.0	1094.8	1182.2
380		686.0	910.5	1032.9	1132.1
390			774.5	949.0	1072.1
400				846.4	998.2

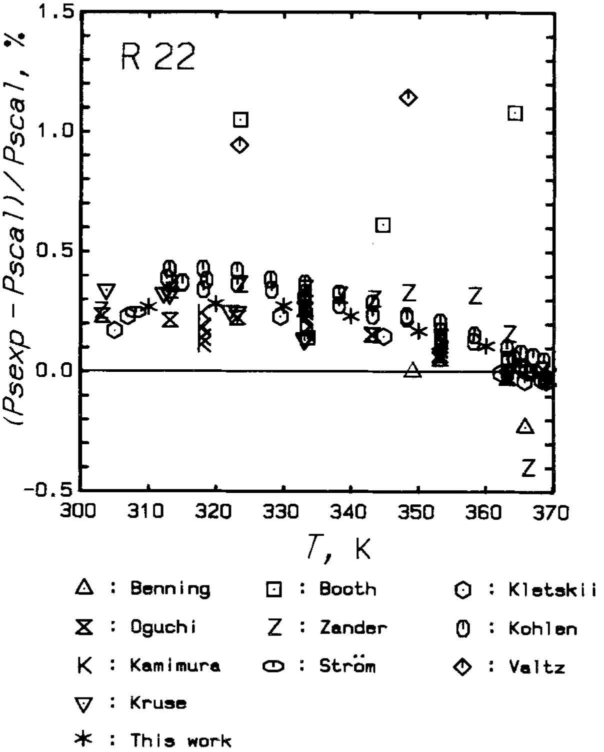

Fig. 1. Comparison of the experimental results for the vapor pressure of R 22 with the values calculated from the correlation proposed by Ashizawa et al. [7].

pressure of the nitrogen gas was measured with an air-piston pressure gauge (Ruska Model 2465), whose precision was assured by the supplier to be 0.010%. The pressure of the nitrogen gas measured is different from that of the sample in the bellows, mainly because of the reaction of the bellows against the compression. Prior to the experiments, this pressure difference was calibrated in the experimental range of temperatures and pressures with an uncertainty of ±0.5 kPa. The uncertainty of the sample pressure measurements was estimated to be less than ±1.0 kPa.

The volume change of the bellows was detected by measuring the bellows displacement with a linear variable differential transformer with a resolution of less than 1 μm. The inner volume of the bellows and its variation with the bellows displacement were calibrated with an uncertainty of ±0.2%.

The mass of each pure component to be mixed was weighed separately with a precision chemical balance (Chyo Model C_2-3000) with an uncertainty of 2 mg. Then the sample was prepared in the supply vessel into

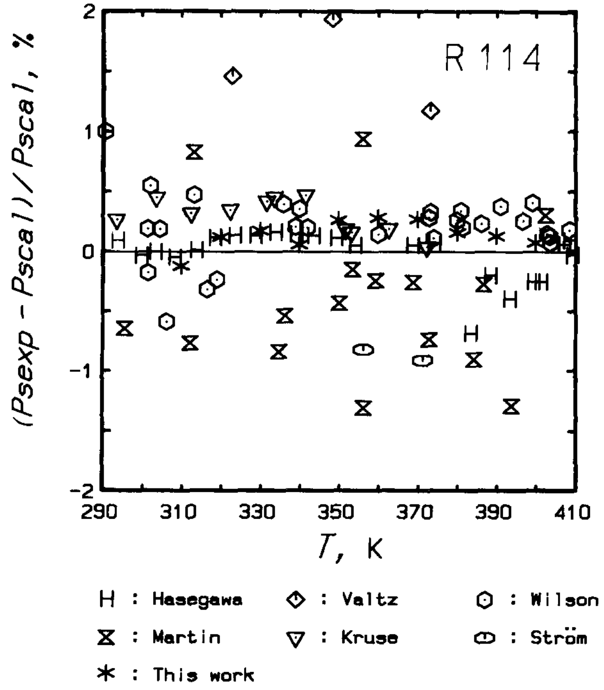

Fig. 2. Comparison of the experimental results for the vapor pressure of R 114 with the values calculated from the correlation proposed by Ashizawa et al. [7].

which each pure component was charged one by one by condensation. The composition of the sample was adjusted at the desired value within ±0.01 %. The total mass and composition of the sample prepared were calculated by these mass measurements with an uncertainty of no greater than ±0.05 %. The sample was then supplied to the bellows, which was evacuated up to around 0.5 mPa, from the supply vessel. The uncertainty in the density measurements was estimated to be no greater than ±0.2 %.

While the temperature of the sample was kept constant, the measurements of the temperature, the pressure, and the bellows position were carried out at small intervals of density to find a breaking point of the isotherm. The values of density and pressure at the breaking point of each isotherm correspond to the saturated liquid density and bubble pressure of the sample, respectively. The uncertainty of these breaking point measurements exceeds those of the sample pressure and density measurements by a factor of 2 to 3. These measurements were performed at several different temperatures for a single composition.

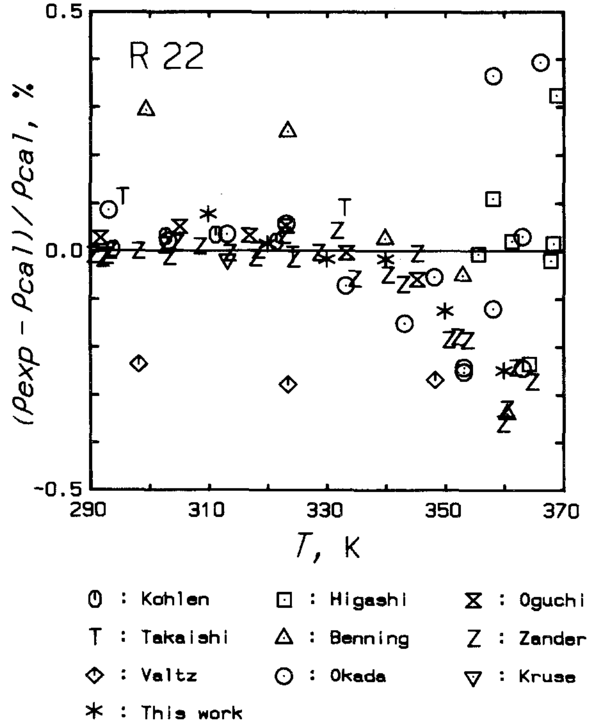

Fig. 3. Comparison of the experimental results for the saturated liquid density of R 22 with the values calculated from the correlation proposed by Okada et al. [17].

3. RESULTS AND DISCUSSION

Experiments have been performed along 10 isotherms between 310 and 400 K for five different compositions, namely, 100, 75, 50, 25, and 0 mol% R 22. The results for the bubble pressures are presented in Table I and for the saturated liquid densities in Table II.

Deviation plots of the experimental vapor pressure data for both pure components from the correlation proposed by Ashizawa et al. [7] are shown in Fig. 1 for R 22 and in Fig. 2 for R 114, respectively. The available literature data [3–6, 8–16] are also shown for comparison. Our R 22 data agree with most literature data [6, 10–13] within ±0.2%. The data of Valtz et al. [3] are systematically higher than our data by about 1%. Those of Kruse et al. [4] and of Ström et al. [5] agree with our data within about ±0.1%. Our R 114 data agree with those of Wilson and Hules [15] and those of Hasegawa et al. [16] within about ±0.5%. The data of Martin [14] deviate from our data with a scatter of about ±1%. The data of Kruse et al. [4] agree with our data within about ±0.5%. The

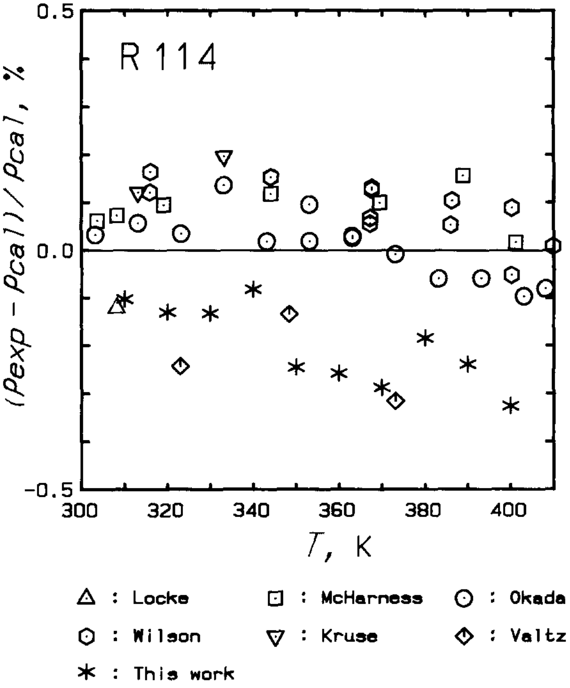

Fig. 4. Comparison of the experimental results for the saturated liquid density of R 114 with the values calculated from the correlation proposed by Okada et al. [17].

data of Valtz et al. [3] are systematically higher than our data by 1–2 %, whereas the data of Ström et al. [5] are systematically lower by about 1.5 %. The greater scatter of the experimental data for R 114 compared with those for R 22 may be attributed to the influence of the isomer.

Deviation plots of the experimental results for the saturated liquid densities of both pure components from the correlation proposed by Okada et al. [17] are shown in Fig. 3 for R 22 and in Fig. 4 for R 114, respectively. The available literature data [3, 4, 9, 10, 12, 13, 15, 17–21] are also shown for comparison. Our R 22 data agree with most literature data [10, 12, 13, 17, 18] within ±0.1 %. The data of Kruse et al. [4] agree with our data within ±0.1 %, whereas those of Valtz et al. [3] are systematically smaller than our data by 0.2–0.3 %. Our R 114 data are systematically smaller than most literature data [15, 17, 21] by 0.2–0.4 %. The data of Valtz et al. [3] agree with our data within about ±0.1 %, whereas those of Kruse et al. [4] are greater than our data by about 0.3 %.

The deviations of the present results for the bubble pressures from Raoult's law are shown in Fig. 5. The R 22 + R 114 system shows positive deviations for temperatures below 340 K and the nonideality increases with

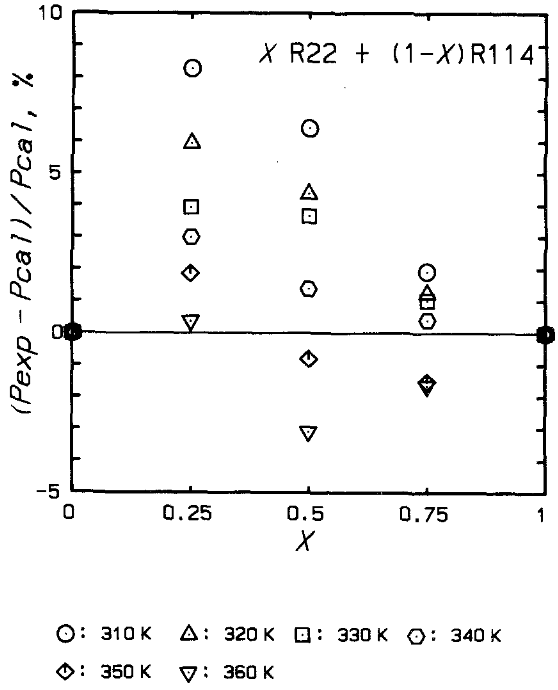

Fig. 5. Deviations of the bubble pressures from Raoult's law.

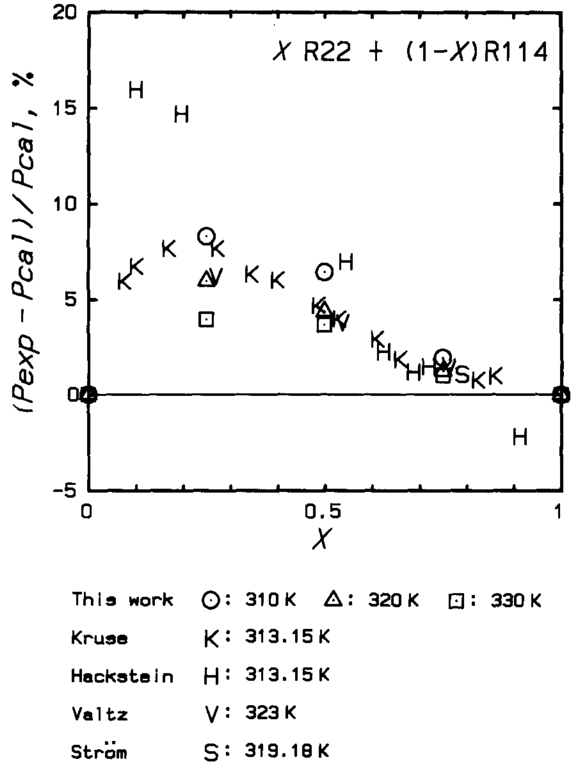

Fig. 6. Comparison of the observed nonideality with that from the available literature data [3–5, 22].

decreasing temperature as Kruse et al. have pointed out [4]. The 25 mol% R 22 mixture shows the maximum nonideality for each temperature. The nonideality of the data along the 350 and 360 K isotherms is very small, but the data of 50 and 75 mol% R 22 mixtures along these two isotherms exhibit negative deviations from Raoult's law. Figure 6 shows the comparison of the nonideality indicated by the present results with that from the available literature data [3–5, 22]. The nonideal behavior of our data is similar to that measured by Valtz et al. [3], Kruse et al. [4], and Ström et al. [5]. The nonideality measured by Hackstein [22] is much larger than indicated by our results.

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