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Thermodynamic Properties of R 22 + R 114 Mixtures in the High-Density Region for Temperatures from 310 to 370 K

H. Fukuizumi[1] **and M. Uematsu**[1]

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The densities for mixtures of R 22 and R 114 have been measured with the variable-volume method using a metal bellows as a function of temperature and pressure. The results for three different compositions (75, 50, and 25 mol% R 22) cover the high-density region along seven isotherms between 310 and 370 K at 15 pressures from 1.0 to 10 MPa. Based on the present density measurements, the values of the excess molar volume, the volume expansion coefficient, and the isothermal compressibility have been calculated. The excess molar volumes for each mixture below 340 K are positive, whereas those above 350 K decrease with decreasing pressure and become negative at low pressures. The behavior of the volume expansion coefficient and the isothermal compressibility for the equimolar mixture are closer to that for R 114 than the average of those for both pure components.

KEY WORDS: density; excess molar volume; isothermal compressibility; refrigerant mixtures; volume expansion coefficient.

1. INTRODUCTION

In three previous publications, we have reported experimental results of several thermodynamic properties for mixtures of R 22 and R 114, i.e., the volumetric properties in the supercritical region [1], the composition dependence of the critical parameters [2], and the bubble pressures and saturated-liquid densities [3]. In this paper, we present experimental densities for three different compositions of this system, namely, 75, 50, and 25 mol% R 22, in the high-density region along seven isotherms between 310 and 370 K at 15 pressures from 1.0 to 10 MPa. The values of the excess

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[1] Department of Mechanical Engineering, Keio University, Yokohama 223, Japan.

molar volume are also reported. 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.

2. EXPERIMENTAL

Densities for mixtures of fixed compositions have been measured at given temperatures and pressures with the variable-volume method using a metal bellows. The apparatus and experimental procedures as well as the results of calibration have been described in detail in a previous publication [4]. We have measured the *PVT* properties and their derivatives for several substances [5–7] by the same apparatus used here. 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 had 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 up to a maximum distance of 16 mm. The volume of the bellows at the reference position was about 27 cm^3. 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 the density values of pure R 22 in the experimental range of temperatures and pressures with an uncertainty of ± 0.2%.

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 with the aid of a thermometer bridge (Tinsley Type 5840). The resistance of the thermometer at the triple point of water was measured periodically. 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 identified with the sample temperature.

The bellows was compressed or expanded by increasing or reducing the pressure of nitrogen gas in the pressure vessel surrounding the bellows. The pressure of the nitrogen gas was measured with two different air-piston pressure gauges (Ruska Models 2465 and 2470), depending on the pressure range. The precision of the two air-piston pressure gauges was assured by the supplier to be 0.015% for high pressures, above 5 MPa, and 0.010% for low pressures, below 5 MPa, respectively. These pressure gauges were used also as devices for generating a constant pressure. Even if the bellows is held in balance, the pressure of the sample in the bellows is different from that of the nitrogen gas surrounding the bellows, mainly because of the elastic force 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 pressure of the sample was set at the desired values within ±2 kPa.

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 a supply vessel into which each pure component was charged one by one by condensation. The composition of the sample was adjusted within ±0.01% of the desired value. 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 to approximately 0.5 mPa, from the supply vessel. The uncertainty in the density measurements was estimated to be within ±0.2%.

3. RESULTS AND DISCUSSION

Experimental results for the density measurements for three different compositions of 75, 50, and 25 mol% R 22 are tabulated in Tables I–III, respectively. The results cover the high-density region along seven isotherms between 310 and 370 K for 15 pressures from 1.0 to 10 MPa. The uncertainties in temperatures and pressures given in Tables I–III were estimated to be less than ±8 mK and ±5 kPa, respectively. We have measured the densities of both R 22 and R 114 at the same state conditions of temperatures and pressures given in Tables I–III by the apparatus used here and reported the results elsewhere [6, 7]. Using these density values, we calculated the excess molar volumes for each mixture at the measured state conditions given in Tables I–III. Here, molar masses of 86.469 $g \cdot mol^{-1}$ for R 22 and 170.922 $g \cdot mol^{-1}$ for R 114 were used for converting densities into molar volumes. The results are tabulated in Tables IV–VI for three mixtures. The uncertainty in the tabulated values of the excess molar volume was estimated to be within ±0.5 $cm^3 \cdot mol^{-1}$. The values of the excess molar volume for each mixture below 340 K are positive, whereas those above 350 K are negative at low pressures and positive at high pressures. These values at constant temperatures above 350 K are decreasing with decreasing pressure. This nonideal behavior is

Table I. Experimental Densities in $kg \cdot m^{-3}$ for a 75 mol% R 22 + 25 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.5	1227.6	—	—	—	—	—	—
2.0	1231.5	1188.3	—	—	—	—	—
2.5	1235.1	1192.8	1145.8	1091.5	—	—	—
3.0	1238.6	1196.9	1151.4	1099.3	1030.7	—	—
3.5	1241.9	1201.1	1156.8	1106.5	1041.8	958.4	—
4.0	1245.1	1205.2	1162.0	1113.3	1051.6	980.6	—
4.5	1248.4	1209.1	1166.9	1119.8	1060.5	994.9	903.8
5.0	1251.4	1212.8	1171.5	1125.7	1068.7	1007.3	927.7
5.5	1254.7	1216.5	1175.8	1131.5	1076.3	1018.3	946.4
6.0	1257.6	1220.0	1180.2	1137.0	1083.4	1028.3	962.1
7.0	1263.4	1226.9	1188.6	1147.1	1096.4	1045.8	987.7
8.0	1268.8	1233.7	1196.2	1156.5	1108.1	1061.0	1008.3
9.0	1274.1	1239.6	1203.5	1165.3	1118.6	1074.4	1025.7
10.0	1279.3	1245.5	1210.5	1173.5	1128.4	1086.5	1041.0

Table II. Experimental Densities in $kg \cdot m^{-3}$ for a 50 mol% R 22 + 50 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.0	1297.1	—	—	—	—	—	—
1.5	1300.4	1260.9	—	—	—	—	—
2.0	1303.7	1264.9	1222.8	1175.6	—	—	—
2.5	1307.0	1268.8	1227.7	1181.9	1126.6	—	—
3.0	1310.4	1272.5	1232.3	1188.0	1134.8	1075.6	—
3.5	1313.4	1276.2	1236.8	1193.8	1142.2	1086.5	1016.9
4.0	1316.4	1279.9	1241.1	1199.1	1149.2	1096.3	1032.4
4.5	1319.4	1283.4	1245.3	1204.1	1155.8	1105.2	1045.7
5.0	1322.2	1286.8	1249.3	1209.1	1162.1	1113.5	1057.4
5.5	1325.1	1290.1	1253.5	1213.9	1167.9	1121.1	1068.0
6.0	1327.8	1293.3	1257.3	1218.5	1173.6	1128.4	1077.7
7.0	1333.1	1299.5	1264.6	1227.1	1184.1	1141.5	1094.7
8.0	1338.4	1305.4	1271.5	1235.5	1193.7	1153.4	1109.6
9.0	1343.4	1311.2	1278.1	1243.1	1202.9	1164.2	1122.8
10.0	1348.2	1316.7	1284.5	1250.3	1211.3	1174.3	1135.0

Table III. Experimental Densities in $kg \cdot m^{-3}$ for a 25 mol% R 22 + 75 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.0	1361.1	1324.7	—	—	—	—	—
1.5	1364.2	1328.3	1290.3	1248.6	—	—	—
2.0	1367.2	1331.8	1294.4	1253.9	1207.8	1156.5	—
2.5	1370.2	1335.3	1298.5	1259.0	1214.1	1165.4	1106.6
3.0	1373.1	1338.6	1302.4	1263.8	1220.0	1173.3	1119.6
3.5	1376.0	1341.9	1306.4	1268.5	1225.8	1180.7	1129.7
4.0	1378.8	1345.0	1310.2	1272.9	1231.3	1187.6	1138.9
4.5	1381.4	1348.3	1313.8	1277.2	1236.5	1194.1	1147.4
5.0	1384.0	1351.3	1317.3	1281.4	1241.8	1200.3	1155.3
5.5	1386.5	1354.3	1320.8	1285.5	1246.7	1206.3	1162.7
6.0	1389.1	1357.1	1324.1	1289.4	1251.2	1212.0	1169.7
7.0	1394.2	1362.9	1330.5	1296.9	1259.8	1222.4	1182.5
8.0	1398.9	1368.2	1336.8	1304.0	1268.1	1232.1	1194.1
9.0	1403.6	1373.5	1342.8	1310.9	1275.8	1241.2	1204.8
10.0	1408.0	1378.5	1348.5	1317.3	1283.1	1249.7	1214.7

Table IV. Excess Molar Volume in $cm^3 \cdot mol^{-1}$ for a 75 mol% R 22 + 25 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.5	0.88	—	—	—	—	—	—
2.0	0.86	0.87	—	—	—	—	—
2.5	0.86	0.87	0.80	—	—	—	—
3.0	0.84	0.87	0.81	0.56	—	—	—
3.5	0.83	0.86	0.81	0.65	−0.04	—	—
4.0	0.82	0.84	0.80	0.70	0.34	—	—
4.5	0.82	0.84	0.80	0.73	0.59	−1.98	—
5.0	0.80	0.84	0.82	0.77	0.74	−0.85	—
5.5	0.78	0.83	0.82	0.79	0.86	−0.23	−6.13
6.0	0.78	0.82	0.83	0.80	0.93	0.15	−2.98
7.0	0.76	0.80	0.80	0.83	1.03	0.58	−0.81
8.0	0.75	0.76	0.81	0.83	1.09	0.80	0.04
9.0	0.74	0.77	0.79	0.83	1.13	0.94	0.48
10.0	0.72	0.75	0.77	0.83	1.16	1.03	0.72

Table V. Excess Molar Volume in $cm^3 \cdot mol^{-1}$ for a 50 mol% R 22 + 50 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.5	1.09	—	—	—	—	—	—
2.0	1.09	1.06	—	—	—	—	—
2.5	1.08	1.06	0.94	—	—	—	—
3.0	1.05	1.06	0.96	0.66	—	—	—
3.5	1.04	1.06	0.98	0.75	−0.11	—	—
4.0	1.02	1.04	0.99	0.83	0.24	—	—
4.5	1.02	1.03	0.99	0.88	0.48	−1.86	—
5.0	1.00	1.03	1.01	0.93	0.64	−0.91	—
5.5	1.00	1.02	0.99	0.96	0.78	−0.34	−5.27
6.0	1.00	1.02	1.00	0.97	0.86	0.02	−2.81
7.0	0.98	1.01	0.98	1.01	0.98	0.46	−0.92
8.0	0.96	1.00	0.98	1.00	1.06	0.70	−0.10
9.0	0.94	0.97	0.98	1.02	1.11	0.86	0.34
10.0	0.93	0.95	0.95	1.02	1.14	0.96	0.59

Table VI. Excess Molar Volume in $cm^3 \cdot mol^{-1}$ for a 25 mol% R 22 + 75 mol% R 114 Mixture

	Temperature (K)						
P (MPa)	310	320	330	340	350	360	370
1.5	0.80	—	—	—	—	—	—
2.0	0.80	0.78	—	—	—	—	—
2.5	0.79	0.78	0.68	—	—	—	—
3.0	0.79	0.78	0.70	0.51	—	—	—
3.5	0.77	0.77	0.70	0.57	−0.07	—	—
4.0	0.75	0.77	0.71	0.61	0.14	—	—
4.5	0.75	0.75	0.71	0.65	0.28	−1.05	—
5.0	0.74	0.75	0.73	0.67	0.35	−0.52	—
5.5	0.75	0.75	0.73	0.69	0.43	−0.21	−2.91
6.0	0.75	0.76	0.73	0.70	0.50	−0.01	−1.60
7.0	0.73	0.74	0.73	0.73	0.59	0.27	−0.55
8.0	0.72	0.74	0.72	0.75	0.64	0.42	−0.08
9.0	0.71	0.72	0.72	0.75	0.69	0.52	0.18
10.0	0.70	0.71	0.70	0.75	0.72	0.60	0.36

consistent with that indicated by the bubble-pressure measurements for the R 22 + R 114 system [3].

We calculated numerically the derivatives of the density with respect to temperature at constant pressure and with respect to pressure at constant temperature from the data given in Tables I–III. Using these derivatives, we calculated the values of the volume expansion coefficient, $\beta = -\rho^{-1}(\partial\rho/\partial T)_P$, and of the isothermal compressibility, $\alpha_T = \rho^{-1}(\partial\rho/\partial P)_T$. By examining the composition dependence of these two properties, it becomes clear that the behavior of the equimolar mixture is much closer to that of R 114 than the average of those for both pure components. Here, as a typical illustration, Fig. 1 shows the composition dependence of the volume expansion coefficient along the 10 MPa isobar, and Fig. 2 shows that of isothermal compressibility along the 350 K isotherm. In these figures, those properties of both R 22 and R 114 from our previous publications [6, 7] are also plotted for comparison.

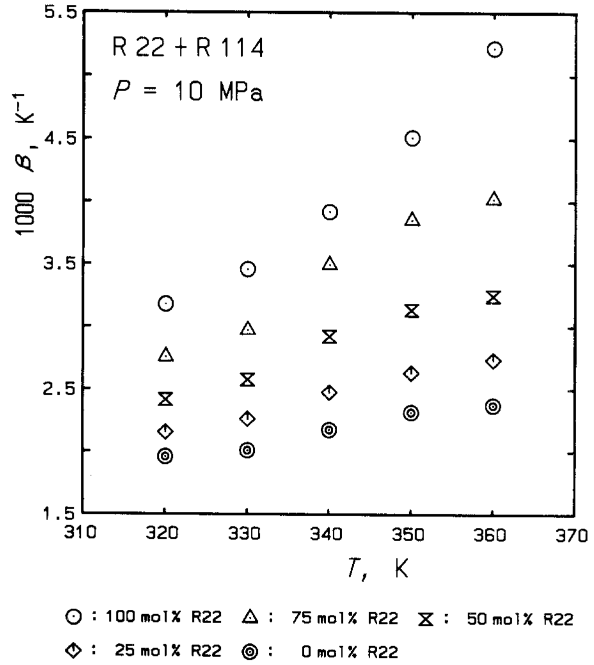

Fig. 1. Composition dependence of the volume expansion coefficient of R 22 + R 114 mixtures along $P = 10$ MPa.

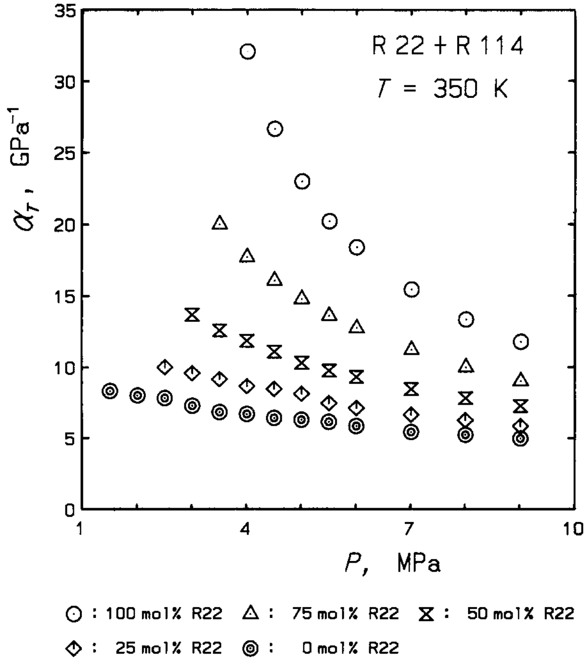

Fig. 2. Composition dependence of the isothermal compressibility of R 22 + R 114 mixtures along $T = 350$ K.

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