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D. R. Defibaugh

National Institute of Standards and Technology

G. Morrison

National Institute of Standards and Technology

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Compressed Liquid Densities, Saturated Liquid Densities and Saturation Pressures of Mixtures Difluoromethane + 1,1,1,2-Tetrafluoroethane Difluoromethane + 1,1-Difluoroethane

Dana R. Defibaugh and Graham Morrison

Thermophysics Division, Chemical Science & Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

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Abstract

The compressed liquid densities and saturation pressures of the mixtures difluoromethane (R32) + 1,1,1,2-tetrafluoroethane (R134a), and difluoromethane (R32) + 1,1-difluoroethane (R152a) have been measured for approximately equimolar mixtures. The liquid densities were measured using a vibrating tube densimeter over a temperature range of 243 K to 373 K and at pressures from near saturation to 6500 kPa. The compressed liquid densities for both mixtures are correlated. The saturation pressures were measured using a vapor-liquid-equilibrium variable-volume sapphire cell with a temperature range from 250 K to the critical temperature. The vapor pressures are correlated, and the equations are presented. Saturated liquid densities were calculated by extrapolating compressed liquid isotherms to the saturation pressure. The saturated liquid densities are correlated and the equations are presented.

Introduction

We have measured the compressed liquid density and vapor pressures of the mixtures, difluoromethane (R32) + 1,1,1,2-tetrafluoroethane (R134a), and difluoromethane (R32) + 1,1-difluoroethane (R152a) over a range of temperatures and pressures where there are no published data. The R32 + R134a mixture had a composition of 0.4980 mole fraction R32. The R32 + R152a mixture had a composition of 0.5066 mole fraction R32.

Here we report measurements in the compressed liquid region along 28 isotherms between 245 K and 372 K, and pressure in the range 1300 kPa and 6500 kPa for mixture R32 + R134a, and between 242 K and 367 K at pressures from 1200 kPa to 6500 kPa for mixture R32 + R152a. The apparatus used to determine density was a vibrating tube densimeter. The densimeter had been calibrated when under vacuum (≈ 1 Pa) and when filled with distilled, degassed water. Details of the calibration can be found in reference [1]. The accuracy of the mixture densities is estimated to be 0.05%. The compressed liquid surfaces (P - ρ) for both mixtures have been correlated and the equations are presented. The correlations represent the compressed liquid density to $\pm 0.02\%$ except in the super critical region.

The saturation pressures for the same mixtures but at slightly different compositions were determined using a variable-volume sapphire cell. The bubble pressure for R32 + R152a ranged from 220 kPa to 4256 kPa which corresponds to temperatures from 249 K to 358 K. Bubble pressures for R32 + R134a were collected between 220 kPa and 4500 kPa corresponding to a temperature range of 250 K to 350 K. The apparatuses and techniques have been described extensively in reference [3]. The critical temperature for both mixtures was determined by the disappearance and reappearance of the meniscus through repeated heating and cooling of the mixture through its critical temperature. Saturation densities were obtained by extrapolating the compressed liquid isotherms to the saturation pressure determined by the VLE apparatus.

Apparatus and Procedure

Mixtures of R32 + R134a and R32 + R152a were prepared on a gas buret by distilling the pure components

into a transfer vessel at liquid nitrogen temperatures. The compositions were determined by weighing the transfer vessel before and after introducing each refrigerant and from the pressure, volume, and temperature conditions prevailing in the gas buret when the sample was prepared. These two quantities typically agreed to within $\pm 0.1\%$. The total liquid volume for the bubble pressure measurements was typically between 2.0 cm^3 to 3.0 cm^3 .

Densimeter

A stainless steel vibrating tube densimeter was used to measure compressed liquid densities. The temperature of the apparatus, shown in figure 1, was regulated by a thermostated water bath. The water bath circulated water/ethylene glycol ($T > 273 \text{ K}$) or methanol ($T < 273 \text{ K}$) through the steel heat exchanger surrounding the vibrating tube. The steel heat exchanger was enclosed in a temperature controlled air bath. A platinum thermometer was used to monitor the temperature of the water exiting the heat exchanger. The temperatures (ITS-90) are accurate to $\pm 0.01 \text{ K}$. The manifold outside the air bath consisted of mercury reservoirs and a mercury manometer separator. A glass capillary in the manometer separator allowed one to locate the mercury level. The manometer itself separated the refrigerant sample from pressurizing argon. The pressure of the system was always maintained above the vapor pressure of liquid in the vibrating tube for temperatures above room temperature. When the vibrating tube was below room temperature, the vapor pressure limit was determined by the temperature of the external manifold. The pressure of the argon was monitored with a quartz pressure transducer. The pressures are accurate to $\pm 0.05 \text{ kPa}$.

Before filling the apparatus, it was rinsed with ethanol and then acetone to remove any residue from previous experiments. The apparatus was then evacuated and cooled to 273 K . Mercury was drawn into the reservoirs and the manometer/separator; the valve connecting the two sides of the separator was closed. Finally, refrigerant sample was condensed into the vibrating tube and separator manifold. Once the sample was loaded, the argon pressure was raised, and the valve separating the sides of the manifold was opened while constantly monitoring the location of the mercury level to assure that the apparatus was indeed completely filled with liquid. Once the apparatus was filled, compressed liquid densities for each mixture were measured.

Variable Volume Sapphire Cell

The saturation pressures were measured with a variable volume sapphire cell. The cell, shown in figure 2, was constructed from a drawn sapphire tube which was closed at both ends with stainless steel plugs and sealed with o-rings. The o-rings were made of neoprene rubber which was compatible with R32, R134a and R152a. The largest

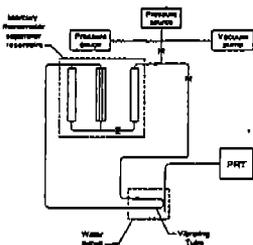


Figure 1: Vibrating tube densimeter apparatus.

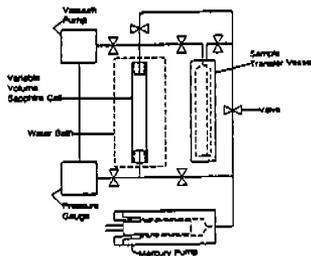


Figure 2: Variable volume sapphire cell apparatus.

volume accessible to the fluid in the cell was 6.5 cm^3 . Smaller volumes were attained by filling the cell partially with mercury. The sample was moved from the transfer vessel to the sapphire cell by displacing it with mercury through the manifold shown in figure 2. During the transfer, the cell was at 273 K and the transfer vessel at 373 K to encourage complete transfer of the material. Sample remaining in the connecting lines and the transfer vessel was collected so that the mass of the sample in the cell was accurately known.

The sapphire cell was immersed in an ethylene glycol-water bath controlled to ± 0.001 K. Measurements of the positions of the vapor-liquid and liquid-mercury menisci, temperatures and pressures were made at 10 K intervals over the range 250 K to the critical temperature of the mixtures. The position of the center of the meniscus and the edge of the meniscus were measured to correct the volumes for meniscus curvature. Temperatures were measured with a 100 ohm platinum resistance thermometer (PRT), which had been calibrated against a standard 25 ohm PRT. Temperatures were accurate to 0.002 K. Pressures were measured with a quartz pressure transducer coupled to the sapphire cell through a mercury separator. Pressures were accurate to 0.5 kPa.

At each temperature, liquid and vapor volumes were measured at two or three total volumes. The set of pressure and liquid volume measurements at each temperature were extrapolated to zero vapor volume to determine the bubble pressure and liquid density. The pressures were accurate to 1 kPa. The volume of the cell at the critical state was used to determine the critical density. Further description of this technique can be found in reference [3].

Results

Compressed Liquid Density

Compressed-liquid-density measurements for the mixtures were made along isotherms between 243 K and 373 K at pressures from 1200 to 6500 kPa. The densities shown in figures 3 and 4 cover the density range from 1.3116

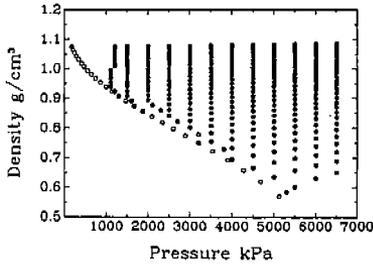


Figure 3: Compressed liquid densities and saturated liquid densities for R32 + R152a mixture.

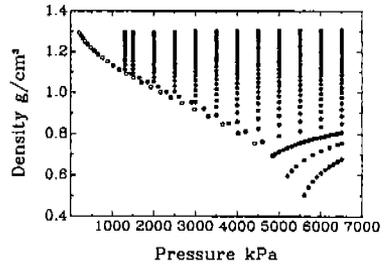


Figure 4: Compressed liquid densities and saturated liquid densities for R32 + R134a mixture.

to 0.5073 g cm^{-3} . The closed circles represent the compressed liquid data, the open circles are saturated liquid densities.

The compressed liquid surfaces for both mixtures were correlated with a function having the form of equation 1 [3]. It reproduces the density of both mixtures to $\pm 0.02\%$ except in the super critical region. Equation 1 is a correlation of only the compressed liquid data. The deviation of the densities from equation 1 for the mixture R32 + R152a is shown in figure 5. Figure 6 is the density deviation plot for mixture R32 + R134a. Both mixtures show scatter greater than $\pm 0.02\%$ at higher temperatures. This scatter is attributed to two factors: the inability of the equation to model highly curved isotherms commonly encountered near the critical point, and the accuracy of the temperature and pressure measurements close to the critical point.

$$\left(\frac{MW}{1000} \frac{P}{RT\rho} \right) - 1 = \sum_{n=1}^8 a_n \rho^n + a_9 \rho^2 \exp(-\rho^2) \quad (1)$$

The temperature dependence of the coefficients is given by:

$$a_1 = b_1 + \frac{b_2}{T_r^{0.5}} + \frac{b_3}{T_r} + \frac{b_4}{T_r^2} + \frac{b_5}{T_r^3}$$

$$a_2 = b_6 + \frac{b_7}{T_r} + \frac{b_8}{T_r^2} + \frac{b_9}{T_r^3}$$

$$a_3 = b_{10} + \frac{b_{11}}{T_r} + \frac{b_{12}}{T_r^2}$$

$$a_4 = \frac{b_{13}}{T_r}$$

$$a_5 = \frac{b_{14}}{T_r^2} + \frac{b_{15}}{T_r^3}$$

$$a_6 = \frac{b_{16}}{T_r^2} + \frac{b_{17}}{T_r^3}$$

$$a_7 = \frac{b_{17}}{T_r^2} + \frac{b_{18}}{T_r^3}$$

$$a_8 = \frac{b_{19}}{T_r^3}$$

$$a_9 = \frac{b_{20}}{T_r^3}$$

R32 + R152a

0.5068 mole fraction R32

$b_1 = 253.99030$
 $b_2 = -7106.7937$
 $b_3 = 665.24009$
 $b_4 = -198.72932$
 $b_5 = 1649.1941$
 $b_6 = 256.14267$
 $b_7 = -994.04921$
 $b_8 = 1610.1714$
 $b_9 = -821.35427$
 $b_{10} = 86.838827$
 $b_{11} = -417.21880$
 $b_{12} = 232.99130$
 $b_{13} = 94.145665$
 $b_{14} = -77.096813$
 $b_{15} = 25.192952$
 $b_{16} = 17.377459$
 $b_{17} = -.89016768$
 $b_{18} = -2.7475538$
 $b_{19} = .39974469$
 $b_{20} = 0.00$

$R = 0.1408365$

$T_c = 370.596 \text{ K}$

$\rho_c = 425.95 \text{ kg/m}^3$

$T_r = T/T_c$

R32 + R134a

0.496 mole fraction R32

$b_1 = 1562.5120$
 $b_2 = -758.28872$
 $b_3 = 9007.7727$
 $b_4 = -5121.7309$
 $b_5 = 44.414941$
 $b_6 = -89.708900$
 $b_7 = 269.17216$
 $b_8 = -274.97956$
 $b_9 = 67.652103$
 $b_{10} = 21.770876$
 $b_{11} = -51.158141$
 $b_{12} = 58.770869$
 $b_{13} = -11.648418$
 $b_{14} = 10.848298$
 $b_{15} = -8.3967063$
 $b_{16} = -1.5917595$
 $b_{17} = -.22535260$
 $b_{18} = 1.1326465$
 $b_{19} = -1.7030075$
 $b_{20} = 7.3009796$

$R = 0.1079428$

$T_c = 363.863 \text{ K}$

$\rho_c = 512.05 \text{ kg/m}^3$

$\rho_r = \rho/\rho_c$

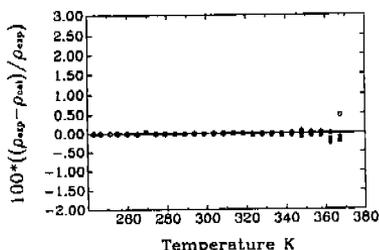


Figure 5: Compressed liquid density difference from equation 1 for R32 + R152a.

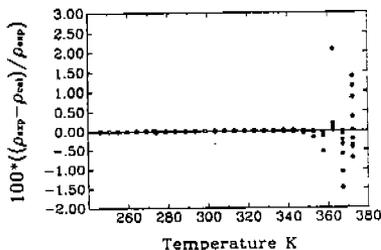


Figure 6: Compressed liquid density difference from equation 1 for R32 + R134a.

Vapor Pressures

Vapor pressure measurements were made between 250 K up to the critical temperature for both mixtures. Each mixture was studied at two slightly different compositions. For the mixture R32 + R134a measurements were made at $x(\text{R32}) = 0.496$ and $x(\text{R32}) = 0.550$; for R32 + R152a, at $x(\text{R32}) = 0.498$ and $x(\text{R32}) = 0.508$. The vapor pressures for each composition were correlated to the following equation, where $T_r = T/T_c$, and T_c is the experimental critical temperature from the sapphire cell measurements.

$$\ln [P / \text{kPa}] = \frac{A_1}{T_r} + A_2 + A_3 T_r + A_4 (1 - T_r)^{1.5} \quad (2)$$

R32 + R152a
 0.508 mole fraction R32
 $A_1 = -7.77256467$
 $A_2 = 17.001803$
 $A_3 = -0.68729628$
 $A_4 = 1.8118925$
 $T_c = 369.462 \text{ K}$

R32 + R134a
 0.55 mole fraction R32
 $A_1 = -7.8747885$
 $A_2 = 17.232101$
 $A_3 = -0.80317518$
 $A_4 = 1.7773332$
 $T_c = 362.620 \text{ K}$

R32 + R152a
 0.498 mole fraction R32
 $A_1 = -7.2345445$
 $A_2 = 16.450808$
 $A_3 = -0.63495592$
 $A_4 = 0.77344192$
 $T_c = 370.596 \text{ K}$

R32 + R134a
 0.496 mole fraction R32
 $A_1 = -7.4333737$
 $A_2 = 16.488353$
 $A_3 = -0.54280573$
 $A_4 = 1.0289872$
 $T_c = 363.863 \text{ K}$

Equation 2 reproduces the saturation pressures to $\pm 0.2 \text{ kPa}$ for each composition listed above. Equation 2 should only be used from 250 K to the critical temperature listed for each mixture.

Isotherms of compressed liquid density were evaluated at the saturation pressure to determine the saturation density. The saturation pressure at each isotherm was determined by correlating the measured bubble pressures of mixtures at nearby compositions with a function of the form of equation 2. These pressures were then interpolated at the relevant temperatures to estimate the pressure of the compositions of the mixtures measured with the densimeter. Finally the saturation pressures were used in equation 1 to determine the saturated liquid densities. The saturated liquid densities for both mixtures were correlated to the following equation where $r = 1 - T/T_c$ (equation 3):

$$\rho = B_1 + B_2 r^{\frac{1}{3}} + B_3 r^{\frac{2}{3}} + B_4 r + B_5 r^{\frac{4}{3}} \quad (3)$$

R32 + R152a
 0.5066 mole fraction R32
 $B_1 = 0.59043543$
 $B_2 = -0.96278322$
 $B_3 = 5.3955338$
 $B_4 = -6.6410635$
 $B_5 = 3.2912390$
 $T_c = 369.621 \text{ K}$

R32 + R134a
 0.498 mole fraction R32
 $B_1 = 0.75998866$
 $B_2 = -1.2759187$
 $B_3 = 6.6636670$
 $B_4 = -8.1132367$
 $B_5 = 4.0202913$
 $T_c = 363.718 \text{ K}$

Equation 3 can reproduce the saturation densities for both mixtures to $\pm 0.03\%$. Equation 3 is traditionally used for pure fluids, however this form was chosen for convenience in correlating the mixture saturation densities. The near-critical region of mixtures is different from that for pure fluids, therefore coefficient B_1 in equation 3 does not represent the critical density of the mixture. Equation 3 should only be used from 250 K to 368 K for the R32 + R152a mixture and to 360 K for the R32 + R134a mixture.

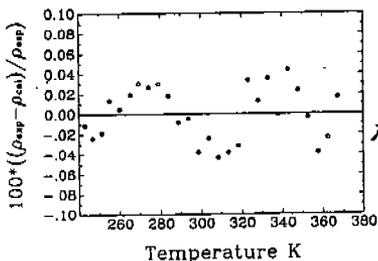


Figure 7: Saturated liquid density difference from equation 3 for R32 + R152a.

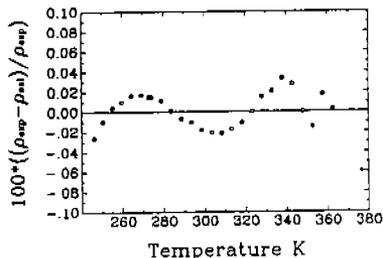


Figure 8: Saturated liquid density difference from equation 3 for R32 + R134a.

Summary

We have measured compressed liquid densities and saturation pressures for the approximately equal molar mixtures R32 + R152a and R32 + R134a. The compressed liquid surfaces (P_ρT) for both mixtures have been correlated and the equations are presented. The vapor pressures for both mixtures were measured from 250 K to their critical temperature. The vapor pressures were correlated so that saturation pressures could be studied at temperatures and compositions where compressed liquid isotherm data were obtained. The saturation pressures and temperatures were used in equation 1 to calculate saturated liquid densities for each mixture. Finally, the saturated liquid densities were correlated and the equation presented. The equations presented in this paper have been chosen only for convenience in correlating large data sets. The functional form of the equations traditionally do not perform well at or near the critical point. Caution should be used when evaluating these equations close to the critical point, and the equations should not be used outside the temperature range given.

Acknowledgements

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