Critical Densities of Pure Fluids from an Intersection Method Assuming Three-Dimensional Ising-like Systems: Application to Refrigerants R32, R124, and R152a **(For Fluid Phase Equilibria)**

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KEYWORDS: critical state; vapour-liquid equilibria; pure; refrigerant R32; refrigerant R124; refrigerant R152a

ABSTRACT

Liquid-vapor coexisting density and temperature data within 3 to 20 K of the critical point at approximately 1 K intervals and critical temperatures obtained in earlier work are used to test a novel method to estimate the critical density (ρ_c) for refrigerants R32, R124, and R152a. The critical density is determined by the intersection, at the critical temperature, of the rectilinear diameter with a function based on maxima in the liquid volume fraction. Functional forms are based on fluids modeled as three dimensional Ising-like systems. For the determination of ρ_c, coexisting densities, temperatures, and the critical temperature are allowed to vary as normally distributed variables about a mean (reported value) with a standard deviation equal to one-third the reported uncertainty. Equally probable data subsets are chosen randomly from the complete data set. Consistent results for ρ_c and its uncertainty are achieved when the data selection - data fitting procedure is repeated one to

two hundred times. Critical densities agree with those in the literature within estimated uncertainties. Uncertainties at a 2σ level for the critical temperatures used and for the critical densities obtained are on the order of 0.3 K and 1.0 kg/m^3, respectively.

INTRODUCTION

Alternative refrigerants such as R32, R124, and R152a, are important as replacements for ozone depleting refrigerants. Knowledge of their coexistence and critical properties is necessary to design new systems using these alternative refrigerants. In this work, we utilize previously obtained critical temperatures and their uncertainties (Van Poolen *et al*. [1]) to test a novel method of obtaining critical densities - the intersection at the critical temperature of the rectilinear diameter and a function based on maxima in the liquid volume fraction ($X_{\ell v}$) . The form of these functions is based on three dimensional Ising-like fluid models.

The saturated liquid density (ρ^{ℓ}), saturated vapor density (ρ^{v}), and temperature (T) data and their respective uncertainties are given for R32 and R152a by Holcomb *et al.* [2] and for R124 by Niesen *et al*. [3]. Of these data, twelve points in the range of 338.24 to 348.61 K for R32, fourteen points in the range of 375.27 to 390.65 K for R124, and thirteen points in the range of 372.35 to 383.71 K for R152a are utilized along with previously obtained critical temperatures to estimate critical densities. The range of temperatures in the data sets is from 3 to 20 K below the critical point temperature. All temperatures are referenced to the ITS-90 temperature scale.

PROCEDURE

The following (truncated) expressions for the coexistence densities based on three dimensional Ising-like fluid systems (see Kiselev and Sengers [4]):

$$\rho^{\ell} = G_1 + G_2\epsilon^{\beta} + G_3\epsilon^{\beta+\Delta_1} + G_4\epsilon^{\beta+2\Delta_1}, \tag{1}$$

and,

$$\rho^{v} = G_1 - G_2\epsilon^{\beta} + G_5\epsilon^{\beta+\Delta_1} + G_6\epsilon^{\beta+2\Delta_1}, \tag{2}$$

where $\epsilon = (T_c\text{-}T)/T_c$, ($\beta = 0.325$ and $\Delta_1 = 0.51$, Kiselev and Sengers [4]) , and G_1 (an estimate for ρ_c) - G_6 are fitted constants, are the basis for the functional forms that follow. The difference in the coexistence densities is:

$$\rho^{\ell} - \rho^{v} = 2G_2\epsilon^{\beta} + (G_3 - G_5)\epsilon^{\beta+\Delta_1} + (G_4 - G_6)\epsilon^{\beta+2\Delta_1}. \tag{3}$$

The rectilinear diameter based on Eqs.(1) and (2) is given as:

$$\frac{\rho^{\ell} + \rho^{v}}{2} = G_7 + G_8\epsilon^{\beta+\Delta_1} + G_9\epsilon^{\beta+2\Delta_1}, \tag{4}$$

where G_7 (estimated ρ_c reported here) - G_9 are separately fitted constants.

The functional form based on maxima in the liquid volume fraction is now developed (see Van Poolen [5]). The liquid volume fraction is:

$$X_{\ell v} = \frac{(\rho_t - \rho^v)}{(\rho^\ell - \rho^v)}, \tag{5}$$

where ρ_t is the total or overall density. For constant values of $\rho_t < \rho_c$, $X_{\ell v}$ goes through a maximum as temperature varies. The appropriate derivative is:

$$\left.\frac{\partial X_{\ell v}}{\partial \epsilon}\right]_{\rho_t} = \frac{(\rho^\ell - \rho^v)(-\frac{d\rho^v}{d\epsilon}) - (\rho_t - \rho^v)(\frac{d\rho^\ell}{d\epsilon} - \frac{d\rho^v}{d\epsilon})}{(\rho^\ell - \rho^v)^2}, \tag{6}$$

and ρ_x (ρ_t for which this derivative is zero (for $T < T_c$), is:

$$\rho_x = \rho^v + \frac{(\rho^\ell - \rho^v)}{1 - \left[\frac{d\rho^\ell}{d\epsilon} \Big/ \frac{d\rho^v}{d\epsilon}\right]}. \tag{7}$$

In the limit $T \rightarrow T_c$, the ratio of derivatives goes to -1 and all the densities go to ρ_c, hence, $\rho_x \rightarrow \rho_c$. Substituting Eqs. (1) and (2) and their derivatives into Eq. (7) yields:

$$\rho_x = G_7 + G_{10}\epsilon^{\beta+\Delta_1} + G_{11}\epsilon^{\beta+2\Delta_1} + G_{12}\epsilon^{\beta+3\Delta_1}, \tag{8}$$

where G_7 (estimated ρ_c reported here) and G_{10} - G_{12} are fitted constants. Critical temperatures and their estimated uncertainties obtained by Van Poolen *et al*. [1] are utilized.

The procedure is to simultaneously fit Eqs. (1), (2), (4), and (8) by the method of least squares. Eqs. (1) and (2) are only used to obtain the derivatives of ρ^ℓ and ρ^v . These

derivatives are utilized in Eq. (7) along with ρ^{ℓ} and ρ^{v} data to provide ρ_x data to be fitted by means of Eq. (8). The reported value of ρ_c is G_7 from the intersection of ρ_d and ρ_x at the critical temperature.

To account for the effect of data choice on the estimate of ρ_c, data subsets are selected for each refrigerant. The six highest temperature data points are always included. Data sets then consist of points that start at randomly selected lowest values (assumed equally probable) and go serially through the six highest temperatures. Values of ρ^{ℓ}, ρ^{v}, T, and T_c are allowed to vary randomly about their mean values (the reported data) as normally distributed variables where the reported uncertainties are assumed three times the standard deviation. These reported experimental uncertainties are 0.5 kg/m^3 for the coexisting densities and 0.1 K for the temperature.

The procedure is repeated between one and two hundred times within one computer run to achieve consistent results for the critical density, which is calculated as an average by,

$$\bar{\rho}_c = \frac{\sum_{i=1}^{n} \rho_{c,i}}{n} , \qquad (9)$$

where n is the number of times the procedure is repeated. Maximum absolute deviations between the data and the fitted equations are below 0.2 %. These differences are essentially random with little evidence of systematic trends.

The standard deviation of ρ_c is estimated by,

$$\sigma_{\rho_{c,n}} = \left[\sum_{i=1}^{n} \frac{(\bar{\rho}_c - \rho_{c,i})^2}{n - 1}\right]^{1/2}. \tag{10}$$

This standard deviation takes into account the reported uncertainty in the data including the dependent variable (temperature and the critical value), deviations that arise from the selected functional form and its ability to fit the data, and the variations that might occur as different data subsets are tested. The reported value for the critical density is,

$$\rho_c = \bar{\rho}_c \pm 2\sigma_{\rho_c}. \tag{11}$$

The method is graphically illustrated (for R32) in Fig. 1.

APPLICATION TO R32

The critical temperature used (Van Poolen *et al*. [1]) is 351.33 ± 0.28 K (at 2σ). The procedure, applied to seven subsets of data between 338.24 and 348.61 K yields, ρ_c = 429.17 ± 1.30 kg/m^3. Literature values (either from direct observation of meniscus behavior or use of a fitted, extrapolated straight line rectilinear diameter) are given and compared to our value in Table 1. Also see Fig. 1. Agreement is within published uncertainties for the majority of the references cited. Where there is disagreement, the upper limit of Schmidt and Moldover [6], 426 kg/m^3, and of Kuwabara *et al*. [7] and Kuwabara *et al*. [8], 425 kg/m^3, differ from our lower limit, 427.87 kg/m^3, by 0.44 percent

and 0.67 percent, respectively.

APPLICATION TO R124

The critical temperature used (Van Poolen *et al*. [1]) is 395.35 ± 0.36 K (at 2σ). The procedure, applied to nine subsets of data between 375.27 and 390.65 K yields, ρ_c = 558.71 ± 0.90 kg/m^3. Literature values (either from direct observation of meniscus behavior or use of a fitted, extrapolated straight line rectilinear diameter) are given and compared to our value in Table 2. Agreement is within published uncertainties.

APPLICATION TO R152a

The critical temperature used (Van Poolen *et al*. [1]) is 386.30 ± 0.24 K (at 2σ). The procedure, applied to eight subsets of data between 372.35 and 383.71 K yields, ρ_c = 368.46 ± 0.64 kg/m^3. Literature values (either from direct observation of meniscus behavior or use of a fitted, extrapolated straight line rectilinear diameter) are given and compared to our value in Table 3. Agreement is within published uncertainties.

CONCLUSIONS

A novel, intersection method is tested for R32, R124, and R152a which yields critical densities from experimental coexistence density data at temperatures where accurate measurements can be accomplished, that is, outside the very near critical region. This method utilizes the thermodynamic behavior of the liquid volume fraction in addition to that of the rectilinear diameter. Values obtained here (by the intersection method) for the critical density (with 2σ uncertainties of about 1.0 kg/m^3) agree with reported literature values with the exception of the two values mentioned above for R32.

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LIST OF SYMBOLS

G	parameter
T	temperature
X	liquid volume fraction

Greek Letters

β	scaling law exponent
Δ_1	scaling law exponent
ρ	density
σ	standard deviation

Subscripts

1,2,...,12	denotes parameters
c	critical point
d	rectilinear diameter
ℓv	liquid volume fraction
lit	literature values
n	number of times the data selection - data fitting procedure is repeated
t	total density
x	density at the maxima in the liquid volume fraction

Superscripts

ℓ	liquid
v	vapor

FIGURE CAPTION

Fig. 1. ρ^{ℓ}, ρ_d, ρ_x, and ρ^v versus temperature for R32

Table 1. Comparison of ρ_c (429.17 ± 1.30 kg/m^3) for R32 from this Study with Literature Values (Critical Temperatures given for Reference).

$T_{c,\,lit}$ (K) (ITS-90)	351.33 - $T_{c,lit}$ (K)	$\rho_{c,lit}$ (kg/m^3)	$\frac{429.17 - \rho_{c,lit}}{\rho_{c,lit}} \times 100$ (%)	Source
351.54 ± 0.20	-0.21	430	-0.19	(Malbrunot *et al.* [9])[2]
351.52 ± 0.02	-0.19	429.61	-0.10	(Singh *et al.* [10])[3]
351.26 ± 0.01	0.07	428 ± 5	0.27	(Higashi [11])[3]
351.24 ± 0.02	0.09	427 ± 5	0.51	(Higashi *et al.* [12])[3]
351.255 ± 0.01	0.09	424 ± 1	1.22	(Kuwabara *et al.* [7])[3]
351.255 ± 0.010	0.075	424 ± 1	1.22	(Kuwabara *et al.* [8])[3]
351.36 ± 0.02	-0.03	419 ± 7	2.43	(Schmidt &Moldover [6])[2]
---	---	428.50 ± 1.83[1]	0.16	(Holcomb *et al*. [2])[2]
351.33 ± 0.28	0.00	429.04 ± 0.50	0.03	(Van Poolen *et al*. [1])[2]

[1] T_c used is 351.54 K from Malbrunot *et al*.[9].
[2] Obtained ρ_c by extrapolation of a straight rectilinear diameter.
[3] Obtained ρ_c by direct observation of meniscus behavior.

Table 2. Comparison of ρ_c (558.71 ± 0.90 kg/m^3) for R124 from this Study with Literature Values (Critical Temperatures given for Reference).

$T_{c,lit}$ (K) (ITS-90)	$395.35-T_{c,lit}$ (K)	$\rho_{c,lit}$ (kg/m^3)	$100\,\frac{558.71 - \rho_{c,lit}}{\rho_{c,lit}}$ (%)	x	Source
395.62 ± 0.05	-0.27	560 ± 2	0.23		(Hirata *et al.* [13] & Kubota *et al*. [14])[2]
395.35 ± 0.03	0.00	566 ± 5	-1.29		(Fukushima &Watanabe [15])[3]
395.36 ± 0.15	-0.01	565 ± 5	-1.11		(Shankland *et al.* [16])[2]
---	---	559.76 ± 1.54[1]	0.19		(Van Poolen *et al.* [17])[2]
395.35 ± 0.36	0.00	560.27 ± 0.56	0.28		(Van Poolen *et al*. [1])[2]

[1] T_c used is 395.62 K from Hirata *et al.* [13].
[2] Obtained ρ_c by extrapolation of a straight rectilinear diameter.
[3] Obtained ρ_c by direct observation of meniscus behavior.

Table 3. Comparisons of ρ_c (368.46 ± 0.64 kg/m^3) for R152a from this Study with Literature Values (Critical Temperatures given for Reference).

$T_{c,\,lit}$ (K) (ITS-90)	386.30-$T_{c,lit}$ (K)	$\rho_{c,lit}$ (kg/m$^{3)}$	$\frac{368.46 - \rho_{c,lit}}{\rho_{c,lit}} \times 100$ (%)	Source
386.62 ± 0.5	-0.32	365 ± 10	0.95	(Mears *et al.* [18])[2]
386.41 ± 0.01	-0.11	368 ± 2	0.13	(Higashi *et al.* [19])[3]
386.32 ± 0.10	-0.02	369 ± 9	-0.15	(Chae *et al*. [20])[2]
---	---	368.81 ± 0.96[1]	-0.09	(Holcomb *et al*. [2])[2]
386.30 ± 0.24	0.00	368.89 ± 0.38	-0.12	(Van Poolen *et al*. [1])[2]

[1] T_c used is 386.41 K from Higashi *et al.* [19]).
[2] Obtained ρ_c by extrapolation of a straight rectilinear diameter.
[3] Obtained ρ_c by direct observation of meniscus behavior.

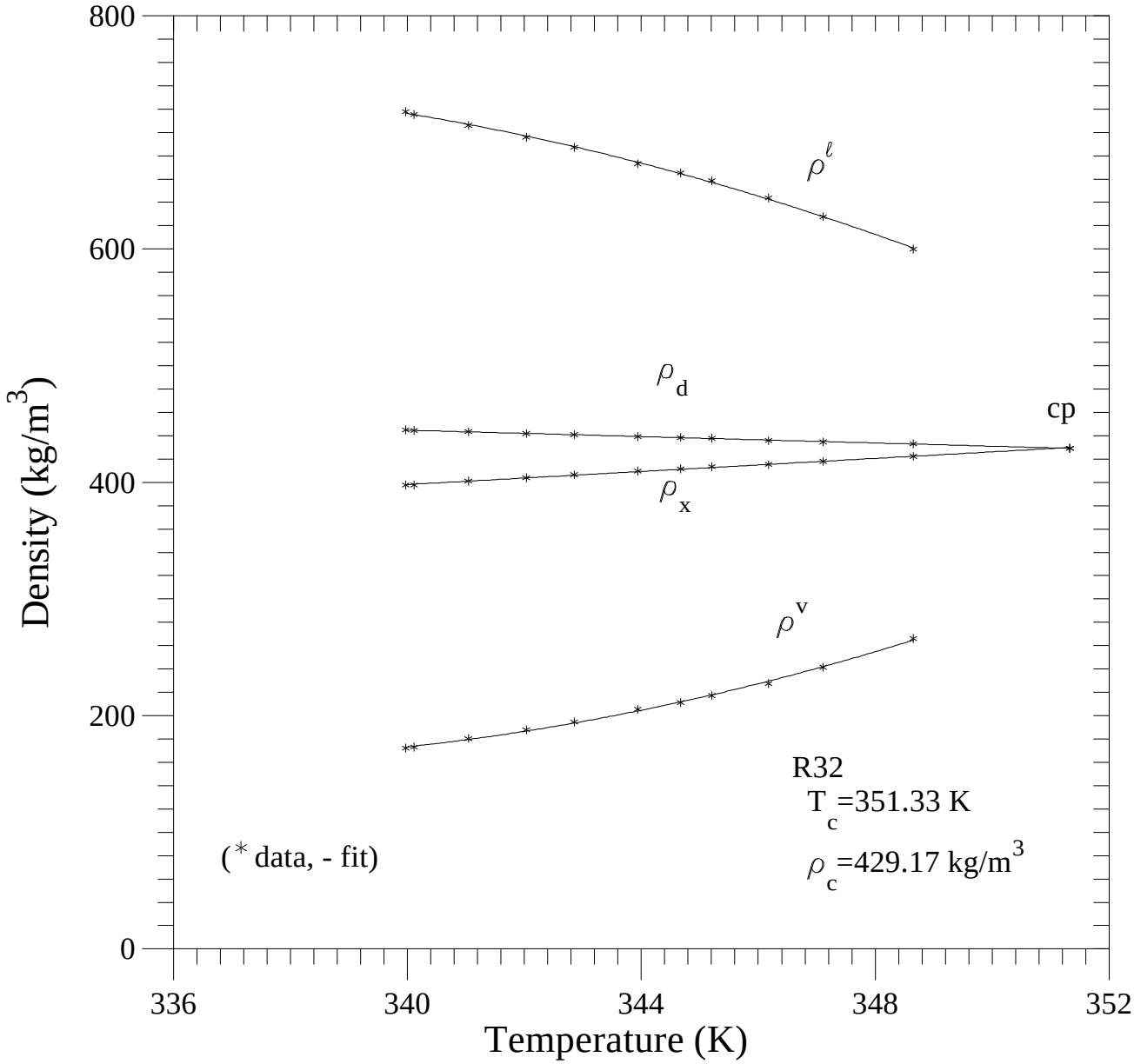
800
600
400
200
0
Density (kg/m3)
336
340
344
348
352
Temperature (K)
ρℓ
ρd
cp
ρx
ρv
R32
Tc=351.33 K
ρc=429.17 kg/m3
(* data, - fit)

Figure 1