



## Experimental study of the isochoric heat capacity of tert-butanol in the critical and supercritical regions

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### ABSTRACT

The one- and two-phase isochoric heat capacities ( $C_V$ ) of tert-butanol in the critical and supercritical regions have been measured with a high-temperature and high-pressure nearly constant-volume adiabatic calorimeter. The measurements were made in the temperature range from 296 K to 524 K for 21 liquid and 7 vapor isochores from  $70.56 \text{ kg m}^{-3}$  to  $763.98 \text{ kg m}^{-3}$ . The isochoric heat capacity jump (quasi-static thermograms supplemented by the sensor of adiabatic control) technique was used to accurately measure of the phase transition parameters ( $\rho_S, T_S$ ) in the critical region. The total experimental uncertainty of density ( $\rho_S$ ), temperature ( $T_S$ ), and isochoric heat capacity ( $C_V$ ) measurements were estimated to be 0.02%, 15 mK, and 2–3%, respectively. The critical temperature ( $T_C = 506.35 \pm 0.2 \text{ K}$ ) and the critical density ( $\rho_C = 268.1 \pm 2 \text{ kg m}^{-3}$ ) for tert-butanol were extracted from the measured saturated properties ( $C_{VS}, T_S, \rho_S$ ) near the critical point. The measured  $C_V$  and saturated density ( $\rho_S, T_S$ ) data near the critical point have been analyzed and interpreted in terms of extended scaling equations for the selected thermodynamic paths (critical isochore and coexistence curve) to accurately calculate the values of the asymptotical critical amplitude ( $A_0^\pm$  and  $B_0$ ). The experimentally derived value of the critical amplitude ratio  $A_0^+/A_0^- = 0.525$  is in good agreement with the value predicted by various scaling theories. The measured thermodynamic properties of tert-butanol near the critical point were also interpreted in terms of the “complete scaling” theory of critical phenomena. In particular, the contributions of the “complete” and “incomplete scaling” terms on the coexistence-curve singular diameter were estimated. The Yang–Yang anomaly of strength parameter  $R_\mu = -0.036$  for tert-butanol was estimated using derived second temperature derivatives of pressure and chemical potential. The measured values of saturated one- ( $C'_{V1}$  and  $C''_{V1}$ ) and two-phase ( $C'_{V2}$  and  $C''_{V2}$ ) liquid and vapor isochoric heat capacities and saturated thermal properties ( $\rho_S, T_S$ ) together with reported vapor–pressure ( $P_S, T_S$ ) data were used to calculate other derived thermodynamic properties such as  $K_T, \Delta H_{\text{vap}}, C_P, C_S, W, (\partial P/\partial T)'_V, (\partial V/\partial T)'_P, (d^2 P_S/dT^2)$ , and  $(d^2 \mu/dT^2)$  of tert-butanol at saturation near the critical point.

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### 1. Introduction

In continuation of previous works on isochoric heat capacity [1–7] of hydrogen-bonded liquids such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, 1-heptanol, and 1-octanol, a study has been made of the tert-butanol (including saturation properties,  $\rho_S, T_S$ ). A survey of the literature reveals that measurements of the thermodynamic properties of tert-butanol are very scarce. No previously reported  $C_V VT$  and saturation properties data on tert-butanol near the critical point. The main objective of the paper is to provide accurate isochoric heat-capacity data in

the two- and one-phase regions near the critical point including coexistence curve ( $C'_{V1}, C'_{V2}, C''_{V1}, C''_{V2}$ ), saturation liquid ( $\rho'_S$ ) and vapor ( $\rho''_S$ ) densities, and critical parameters ( $T_C, \rho_C$ ) for tert-butanol. We also provided comprehensive analysis of the available experimental critical and saturated property data and correlations for tert-butanol to estimate the reliability and consistency of the published datasets.

#### 1.1. Saturated-liquid and -vapor densities and vapor pressure data and correlations

Ambrose and Townsend [8] reported vapor pressure data for tert-butanol (purity of 99.96 mass%) in the temperature range from 376.42 K to 506.15 K using vertical glass tube connected with an oil-operated, dead-weight piston-gauge via a mercury-filled U tube. The sample was confined over mercury, and position of the

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sample-mercury interface was determined accurately by means of a cathetometer. Uncertainty of the vapor pressure measurements is 0.004 atm. The measured vapor pressures were fitted to equation

$$\log P_S = A' - \frac{B}{(C+t)} - Dt + E(t-F)^3, \quad \text{at } t > 375.15 \text{ K} \quad (1)$$

and

$$\log P_S = A - \frac{B}{(C+t)}, \quad \text{at } t < 375.15 \text{ K}, \quad (2)$$

where  $A=4.32536$ ;  $B=1094.341$ ;  $C=170.658$ ;  $D=0.00026$ ;  $E=2.095 \times 10^8$ , and  $A'=4.35499$ . The vapor pressure equation determined by Krone and Johnson [9] from experimental data was as

$$\ln P_S = 39.7545 - \frac{10456}{T} - 3.215 \ln T \quad (3)$$

Krone and Johnson [9] used the literature  $C_p$  data [10,11] and own vapor–pressure and  $PVT$  measurements for tert-butanol to calculate derived thermodynamic properties at saturation (saturation vapor and liquid densities, enthalpies, and entropies).

Ambrose and Townsend [8] used the same apparatus to measure orthobaric density (sealed tube technique). They used 15 cm long glass tube. The derived orthobaric densities were fitted to equations

$$\rho'_S + \rho''_S = 2\rho_C + a(t_C - t) - b(t_C - t)^2, \quad (4)$$

$$\rho'_S - \rho''_S = c(t_C - t)^{1/3} - d(t_C - t)^2, \quad (5)$$

where  $a=0.00132$ ;  $b=0.8 \times 10^6$ ;  $c=0.1308$ ;  $d=0.96 \times 10^6$ .

Costello and Bowden [12] measured saturated liquid and vapor densities for series alcohols over ranges of temperature below and above the boiling point (from 313 K to 413 K for tert-butanol). Measurements were made with a sealed dilatometer. No uncertainty of the measured densities was provided by the authors. They showed that the variation of orthobaric density difference,  $(\rho'_S - \rho''_S)$ , with temperature may be represented by the equation

$$\rho'_S - \rho''_S = d_0 \left(1 - \frac{T}{T_C}\right)^m, \quad (6)$$

where  $m=0.231$  and  $d_0=0.9376$  at temperatures from 313 K to 353 K;  $m=0.213$  and  $d_0=0.9508$  at temperatures from 353 K to 413 K; and  $m=0.218$  and  $d_0=0.9590$  at temperatures from 313 K to 413 K. Dannhauser and Bahe [13] reported saturated liquid densities of tert-butanol from 300 K to 500 K. Measurements were made with dilatometers which were constructed from precision-bore capillary tubing with a thick wall bulb blown on one end. The dilatometers were suspended in a mechanical convection oven and thermocouples, taped to the stem near the bulb, were used to monitor the temperature. No uncertainty of the measured densities was provided by the authors. Owen et al. [14] reported saturated liquid densities of tert-butanol at temperatures from 298 K to 338 K. The authors are not provided the method and uncertainty of the density measurements. Kuss [15] has measured the saturated liquid densities of tert-butanol at temperatures from 293 K to 323 K. Low temperature (below 313 K) measurements of saturated liquid densities were done by several authors [16–18]. This range is not overlap with the present temperature range. Three data points for the saturation liquid densities were reported by Smyth and Dornte [19] at temperatures from 303 K to 343 K. Only three datasets reported by Ambrose and Townsend [8], Krone and Johnson [9] (derived values), and Costello and Bowden [12] are available in the literature for the saturated vapor densities in the temperature range from 313 K to 480 K.

**Table 1**  
Reported values of the critical properties of tert-butanol.

$T_C$ (K)	$P_C$ (MPa)	$\rho_C$ (kg m <sup>-3</sup> )	References
506.215	3.972	270.00	Ambrose and Townsend [8]
508.916	4.232	258.36	Krone and Johnson [9]
508.160			Pawlewski [21]
506.35	–	268.10	This work

Saturated-vapor densities can be calculated using second virial coefficient data [20] and vapor pressures data by Ambrose and Townsend [8] as

$$\rho''_S(T) = -\frac{0.5}{B} - \left(\frac{0.25}{B^2} + \frac{P_S}{BRT}\right)^{1/2}, \quad (7)$$

where experimental second virial coefficients reported by Cox [20] were fitted to the equation

$$B = 54.4804 - \frac{2.904513 \times 10^4}{T} + \frac{522.2542865 \times 10^6}{T^3} \quad (8)$$

In Eq. (8)  $T$  in K and  $B$  in cm<sup>3</sup> g<sup>-1</sup>. These equations, (7) and (8), were used to calculate saturated-vapor densities for tert-butanol at low temperatures (below 323 K).

## 1.2. Equation of state

Krone and Johnson [9] developed Beattie–Bridgeman type equation of state for tert-butanol

$$P = \frac{RT}{v^2} \left(1 - \frac{c}{vT^3}\right) \left[v + B_0 \left(1 - \frac{b}{v}\right)\right] - \left(\frac{A_0}{v^2}\right) \left(1 - \frac{a}{v}\right) \quad (9)$$

where  $a=0.145$ ;  $A_0=20$ ;  $b=0.081$ ;  $B_0=0.070$ ; and  $c=3 \times 10^7$ .

## 1.3. Critical parameters

Very restricted (only three) critical parameter datasets are available for tert-butanol (see Table 1). Ambrose and Townsend [8] measured the critical temperature, the critical density, and the critical pressure of the tert-butanol sample using visual method (observation of the disappearance and reappearance of the meniscus). They recommended the following values of the critical parameters for tert-butanol:  $T_C=506.215$  K,  $P_C=3.972$  MPa, and  $\rho_C=270.00$  kg m<sup>-3</sup>. The derived value of the critical temperature is mean value of a series of observations on the disappearance and reappearance of the meniscus. Taking all factors into account, the authors claimed uncertainty of the critical temperature measurements is 0.2 K. The value of the critical temperature for tert-butanol was obtained from different tubes. The value of the critical pressure was measured several times with more than one filling of the experimental tube. The uncertainty of the critical pressure measurement is 0.1%. The critical density was obtained by extrapolation of the rectilinear diameter to the critical temperature, although that the rectilinear diameter is in fact curved, and the extrapolation may be subject to considerable personal variation (see below Section 5). Krone and Johnson [9] also used critical disappearance meniscus and opalescence technique to measure of the critical temperature of tert-butanol (purity was 99.8 mol%). The derived values of the critical temperature is  $T_C=508.916$  K. The critical pressure  $P_C=4.232$  MPa was obtained by extrapolation of the vapor–pressure equation to the critical temperature. The critical density derived by Krone and Johnson [9] from saturated density data is 258.36 kg m<sup>-3</sup> which lowers than Ambrose and Townsend [8] measurements by 4.5%. The value of the critical temperature  $T_C=508.15$  K derived by Pawlewski [21] is close to the value reported by Krone and Johnson [9], while considerable (by 1.935 K) differ from the Ambrose and Townsend [8] value.

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