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Experimental study of the *PVT* and $C_V VT$ properties of *n*-butanol in the critical region

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ABSTRACT

The *PVT* and $C_V VT$ properties of *n*-butanol have been measured in the near- and supercritical regions. Measurements of *PVT* relation for *n*-butanol was made along 6 liquid and vapor near-critical isochores in the density range from (113.76 to 470.00) kg m^{-3} and at temperatures from (497 to 616) K and at pressures up to 10 MPa. The measurements were performed with a constant-volume piezometer technique. Caloric ($C_V VT$) properties of *n*-butanol were measured along the critical isochore and coexistence curve (liquid and vapor branches) in the one- and two-phase regions. The temperatures, densities, and pressures at the liquid-gas boundary curve (P_S, T_S, ρ_S) and the critical parameters ($T_C = 563.05 \pm 0.2$ K, $P_C = 4.405 \pm 0.01$ MPa, $\rho_C = 270.0 \pm 2$ kg m^{-3}) for *n*-butanol were obtained using the isochoric (*P*–*T*) break-point and quasi-static thermograms (C_V jumps) techniques. The expanded uncertainty of the density, pressure, and temperature measurements at the 95% confidence level with a coverage factor of $k = 2$ is estimated to be 0.10% (at high densities) to 0.12% (at low densities), 0.0005–0.005 MPa, and 15 mK, respectively. The total experimental uncertainty of isochoric heat capacity (C_V) measurements were estimated to be 2–3%. The measured C_V, *PVT*, saturated density (ρ_S, T_S) and vapor-pressure (P_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, critical isotherm, and coexistence curve) to accurately calculate the values of the asymptotic critical amplitudes ($A_0^{\pm}$, $\Gamma_0^{\pm}$, D_0, B_0) and to check their universal ratios. The measured saturated density data of *n*-butanol near the critical point were also interpreted in terms of the "complete scaling" theory of critical phenomena. In particularly, the contributions of the "incomplete", $B_2 t^{1-\alpha}$, and "complete scaling", $B_4 t^{2\beta}$, terms on the coexistence-curve singular diameter were estimated. The values of the asymmetry parameters a_3 and b_2 of the coexistence curve singular diameter have been calculated. The strength of the Yang-Yang anomaly R_μ for *n*-butanol was estimated using asymmetry parameters a_3 and the contributions of the second temperature derivatives of vapor-pressure, ($\mathrm{d}^2 P_S/\mathrm{d}T^2$), and chemical potential, ($\mathrm{d}^2\mu/\mathrm{d}T^2$), in the singularity of two-phase isochoric heat capacity, C_{V2}. The measured values of saturated one- (C_{V1}', C_{V1}'') and two-phase (C_{V2}', C_{V2}'') liquid and vapor isochoric heat capacities and saturated density data (ρ_S, T_S) together with measured vapor-pressure (P_S, T_S) data were used to calculate other derived thermodynamic properties, such as K_T, ΔH_{vap}, C_P, C_S, W, $(\partial P/\partial T)_V'$, $(\partial V/\partial T)_P'$, ($\mathrm{d}^2 P_S/\mathrm{d}T^2$), and ($\mathrm{d}^2\mu/\mathrm{d}T^2$) of *n*-butanol at saturation near the critical point. The results were compared with the direct measurements of these properties.

1. Introduction

In continuation of previous works on isochoric heat capacity [1–10] of alcohols (methanol, ethanol, *n*-propanol, iso-propanol, *n*-butanol, iso-butanol, sec- and tert-butanol, *n*-hexaanol, *n*-heptanol, and *n*-octanol, a study has been made of the *n*-butanol, including *PVT* and saturation properties (ρ_S, T_S) near the critical point. A survey of the literature reveals that measurements of the thermodynamic properties of *n*-butanol in the critical and supercritical regions are very scarce. Preliminary measurements of the $C_V VT$ and saturated density properties of *n*-butanol have been reported in our previous publications [7,11]. The main objective of the present work is to provide new accurate *PVT* and two- and one-phase isochoric heat-capacity data in the sub- and supercritical regions, including coexistence curve (C_{V1}', C_{V1}'', C_{V2}', C_{V2}''), saturation liquid (ρ_S') and vapor (ρ_S'') densities, and critical parameters (T_C, ρ_C) for *n*-butanol. We also provided comprehensive analysis of the available experimental critical and saturated property data

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Table 1
Reported critical properties of *n*-butanol.

Year	Reference	T_C (K)	P_C (MPa)	ρ_C (kg m^{-3})
1883	Pawlewski [67]	560.33	–	–
1888	de Heen [68]	543.68	–	–
1923	Herz and Neukirch [69]	–	4.904	–
1943	Fischer and Reichel [70]	561.18	–	–
1953	Donham [61]	562.89	4.416	267.2
1953	Kobe and Lynn [83]	561.15	4.965	–
1955	Golik et al. [71]	560.23	–	–
1955	Kay and Donham [48]	562.95 ± 0.05	4.415 ± 0.003	267 ± 6
1955	Singh and Shemilt [47]	560.13 ± 0.05	4.924 ± 0.050	270 ± 2
1958	Ravikovich and Solomko [73]	564.00	–	–
1960	Mocharnyuk [72]	560.23	–	–
1963	Ambrose and Townsend [41]	563.04 ± 0.10	4.413 ± 0.004	269.9
1964	Skaates and Kay [42]	563.05 ± 0.22	4.413 ± 0.007	275 ± 3
1966	Efremov [43]	561.03	–	271.00
1971	Suleimanov [54]	561.14	–	263.16
1974	Young [74]	562.16	–	–
1979	Grigor'ev et al. [82]	561.00	4.160	–
1980	Naumova et al. [75]	563.01	–	269.54
1982	Vasil'eva and Tyvina [76]	563.06	–	–
1985	Zolin et al. [40]	562.98	–	270.00
1986	Christou and Young [77]	563.06	–	–
1988	Christou [78]	563.06	–	–
1989	Rosenthal and Teja [79]	562.40 ± 0.6	4.418 ± 0.020	–
1990	Lydersen and Tsochev [109]	563.60	4.410	–
1994	Shakhverdiev et al. [33]	562.17	4.391	270.2
1995	Gude and Teja [80]	563.00 ± 0.3	4.414 ± 0.020	271 ± 3
2003	Bashirov [110]	563.05	4.424	–
2008	Bogomol'nyi [81]	562.90	–	–
2010	Alekhina et al. [166]	563.00	–	–
2012	This work[a]	563.05 ± 0.02	–	270 ± 1
2012	This work[b]	562.95 ± 0.3	4.405	270 ± 3

[a] From C_V measurements.
[b] From *PVT* measurements.

and correlations for *n*-butanol to estimate the reliability and thermodynamically consistency of the published datasets. *n*-Butanol is also very important fluid for technological applications. For example, supercritical *n*-butanol as other alcohols (methanol, ethanol, *etc.*) can be used for transesterification of the vegetable oils in supercritical media [12,13]. It is well-known that addition of a polar co-solvent to supercritical carbon dioxide often leads to an enhancement in the solubility of a solvent and improving the selectivity of CO_2 [14]. Alcohols used as modifiers for CO_2 in SCF extraction processes to modify the polarity and solvent strength of the primary SCF, therefore minimize operating costs in an extraction processes [14–17].

Isochoric and *PVT* measurements near the critical point are also very important for scientific applications (for fundamental studies). Isochoric heat capacity is a key thermodynamic property (very sensitive tool) for study of the phase-transition and critical phenomena. Its first density derivative, $(\partial C_V/\partial \rho)_T$, provide valuable information on temperature derivatives of the thermodynamic functions of compressed fluids. For example, the slopes of one-phase C_V–ρ isotherms are directly related with the second temperature derivative, $(\partial^2 P/\partial T^2)_\rho$ (see below Section 4.3.2), which is cannot be accurately calculated by twice differentiating of the equation of state or directly measured, even very precise, *PVT* data. The slopes of two-phase (C_{V2}–V) isotherms are also gives information on the values of second temperature derivative of the vapor pressure, $T(\mathrm{d}^2P_S/\mathrm{d}T^2)$, while the intercepts for $V=0$ are related with $-T(\mathrm{d}^2\mu/\mathrm{d}T^2)$ (see below Section 4.2.1). Accurate C_V and *PVT* data near the critical point are also needed to calculate the universal critical exponents (α, β, γ, δ), universal ratios between the asymptotic (A_0^-/A_0^+, $A_0^+\Gamma_0^+B_0^2$, $D_0\Gamma_0^+B_0^{\delta-1}$, Γ_0^+/Γ_0^-) and non-asymptotic (A_1^+/Γ_1^+, A_1^+/B_1) critical amplitudes, to establish accuracy of the scaling theories and their predictions, and to check the crossover model parameters [18–27]. Accurate experimental isochoric heat capacity and singular diameter data near the critical point for pure fluids are also need to confirm the conclusions and basic idea and physical bases of a "complete" scaling theory of critical phenomena [28–30]. A new, $B_4t^{2\beta}$, non-analytical contribution of liquid-gas asymmetry ("complete" scaling term or 2β anomaly) of the singular diameter and the strength of Yang-Yang anomaly, R_μ (contribution of the $(\mathrm{d}^2\mu/\mathrm{d}T^2)$ and $(\mathrm{d}^2P_S/\mathrm{d}T^2)$ in singularity of two-phase C_{V2} at the critical point) was found using the accurate isochoric heat capacity measurements [28–32]. In this work we simultaneously measured one- and two-phase isochoric heat capacity of *n*-butanol along the critical isochore and liquid-gas coexistence curve, and liquid and vapor saturation densities near the critical point to check the basis "complete" scaling theory conclusions and Yang-Yang anomaly strength R_μ for *n*-butanol. We also provided for *n*-butanol precise *PVT* measurements in the critical and supercritical regions to calculate the asymptotic critical amplitudes, such as B_0, D_0, Γ_0^+, Γ_0^-, which are, together with critical amplitudes for caloric properties (A_0^-, A_0^+), can be used to check the universality of the critical amplitude ratios.

2. Literature review of available experimental thermodynamic data for *n*-butanol

2.1. *PVT* properties and equation of state

Thermodynamic property data for *n*-butanol in the near-critical and supercritical conditions are very restricted. The largest gap in the data base is found *PVT*, C_VVT, and other thermodynamic properties measurements in the near- and supercritical regions for *n*-butanol. Most of the reported *PVT* data cover the temperature and pressure ranges below the critical point (basically in the liquid phase at temperatures to 363 K and pressures up to 35 MPa, NIST/TRC database review results). Here we will briefly review