Experimental Study of the Isochoric Heat Capacity and Coexistence-Curve Singular Diameter of s-Butanol near the Critical Point and Yang-Yang Anomaly Strength

Laritta Radzhabova[C] and Gennady Stepanov
Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Fluid Theories and Critical Phenomena Laboratory, Makhachkala, Dagestan, Russia
radzhabova.l@mail.ru

Ilmutdin Abdulagatov[S]
Geothermal Research Institute of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Daghestan, Russia

The one- and two-phase isochoric heat capacities (C_v) of s-butanol near the critical point have been measured with a high–temperature and high–pressure nearly constant–volume adiabatic calorimeter. The measurements were made in the temperature range from 304 K to 551 K for 22 liquid and vapor isochores from 76.44 kg×m^{-3} to 794.06 kg×m^{-3}. The isochoric heat capacity jump (quasi-static thermograms supplemented by the sensor of adiabatic control) technique have been used to accurately measure of the phase transition parameters (T_s, ρ_s). The total experimental uncertainty of density (ρ), temperature (T), and isochoric heat capacity (C_v) were estimated to be 0.06 %, 15 mK, and 2 % to 3 %, respectively. The critical temperature (T_c=535.95 K) and the critical density (ρ_c=276.40 kg×m^{-3}) for s-butanol were determined from the measured saturated properties (C_v, T_s, ρ_s) near the critical point. The measured (C_v) and saturated density (T_s, ρ_s) data near the critical point have been analyzed and interpreted in terms of extended scaling type equations for the selected thermodynamic paths (critical isochore and coexistence curve) to accurately calculate the values of the asymptotical critical amplitudes of heat capacity ($A_0^{\pm}$) and coexistence curve (B_0). The measured thermodynamic properties (C_v, T_s, ρ_s) of s-butanol near the critical point were also interpreted in the terms of “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. We determined the values of the asymmetry parameters a_3 and b_2 of the coexistence curve singular diameter. The strength of the Yang-Yang anomaly R_m for s-butanol was estimated using asymmetry parameters a_3 and the contribution of the second temperature derivative of vapor-pressure and chemical potential in the singularity of two-phase C_{v2}.