

Critical Behavior of the Isochoric Heat Capacity of an Aqueous Ammonia Mixture

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The isochoric heat capacity of a (0.25 mole fraction of ammonia) $\text{H}_2\text{O}+\text{NH}_3$ mixture has been measured in the near- and supercritical regions. Measurements were made in the one- and two-phase regions including the coexistence curve using a high-temperature, high-pressure, nearly constant-volume adiabatic calorimeter. Temperatures at the phase transition curve, $T_S(\rho)$, for each measured density (isochore) and the critical parameters (T_C and ρ_C) for the $0.75\text{H}_2\text{O}+0.25\text{NH}_3$ mixture were obtained using the method of quasi-static thermograms. The expanded uncertainties of the heat-capacity measurements at the 95 % confidence level with a coverage factor of $k=2$ are estimated to be 2 % to 3 % in the near-critical and supercritical regions, 1.0 % to 1.5 % in the liquid phase, and 3 % to 4 % in the vapor phase. Uncertainties of the density, temperature, and concentration measurements are estimated to be 0.06 %, 15 mK, and $5 \cdot 10^{-5}$ mole fraction, respectively. The uncertainty of the phase transition and the critical temperature values was 0.02 K. The measured isochoric heat capacities, saturated densities, and critical parameters were compared with the data reported by other authors and values calculated from an equation of state. The value of the Krichevskii parameter was calculated using the critical properties data for the mixtures and vapour pressure value at the critical point for pure solvent (H_2O). The derived value (48.2 ± 3 MPa) of the Krichevskii parameter was used to analyze the critical behaviour of the strong (C_P , K_T) and weakly (C_V) singular properties (in terms of the principle of isomorphism of critical phenomena in binary mixtures). The values of the characteristic parameters (K_1, K_2), temperatures (τ_1 , τ_2), and the characteristic density differences ($\Delta\rho_1$, $\Delta\rho_2$) were calculated for the $\text{H}_2\text{O} + \text{NH}_3$ mixture by using the critical-curve data. The prediction of the critical behavior of the isochoric heat capacity along the critical isochore for the $\text{H}_2\text{O} + \text{NH}_3$ mixture was compared with the directly measured values.