Thermodynamic Properties of Multicomponent Mixtures near the Liquid-Vapor Critical Point

Mikhail Belyakov [S], Vitalii Voronov, Evgenii Gorodetskii [C] and Viatchesla Kulikov
Oil&Gas Research Institute, Russian Academy of Sciences, Moscow, Russia

The study of near-critical thermodynamic behavior of multicomponent liquid mixtures presents great interest for better comprehension of critical phenomena in complex systems as well as for many practical applications also. This work includes the results of our research of methane-propane-pentane ternary mixture in the vicinity of the liquid-vapor critical point. A highly-precise adiabatic calorimeter was used to measure the temperature dependencies of the pressure and the enthalpy along ten different isochores at fixed mixture composition both in the one- and two-phase regions. The isochoric heat capacity and the temperature derivative of the pressure have been calculated by means of the numerical differentiation of the corresponding experimental dependencies upon the temperature. As a result the isochoric heat capacity for near-critical isochores exhibits the well- known cusp-like behavior. Moreover, for the first time it has been demonstrated that the temperature derivative of the pressure for near-critical isochores also reveals the anomalous behavior in contrast to one-component fluids. To describe the obtained experimental data a new approach permitting the elaboration of the equation of state of multicomponent mixture in the vicinity of liquid-vapor critical point has been formulated. The proposed approach is based on the scaling theory, hypothesis of mixing of thermodynamic fields originally formulated for one-component fluids and isomorphism hypothesis. It has been shown that various thermodynamic properties in the critical region can be parameterized in terms of two independent variables of the scaling theory. The set of such parameterizations specifies the equation of state of a liquid mixture near the critical point. In addition it is essential that the form of the derived expressions of thermodynamic properties does not depend on the number of components in mixture. The model of the equation of state has been tested on the mixture experimental data. As a result, the equation of state of the mixture was obtained. The use of this equation of state allows us to calculate with the high accuracy various thermodynamic properties including dew-bubble curves in the broad vicinity of the mixture critical point.