New Terms for Use in Helmholtz Energy Equations of State for the Associating Fluids: Methanol, Ethanol, 1-Propanol, 2-Propanol, and Ammonia

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Associating phenomena occur because of hydrogen bonding, the strength of the dipole moment of polar molecules, and coordination bonding. Methanol, ethanol, 1-propanol, 2-propanol, and ammonia can form multimers as a result of hydrogen bonding, which causes unique behavior in their thermodynamic properties, for example: higher critical temperatures, strongly increasing isobaric and isochoric heat capacities in both liquid and vapor phases, more pronounced virial coefficient behavior at low temperatures, increased partial differentials of pressure with respect to temperature and density as shown by the phase identification parameter, and so on. Alcohols and ammonia are very important industrial fluids. Alcohols can be used as industrial raw materials, fuels, solvents, detergents, disinfectants, extracting agents, etc. Ammonia is an environmentally friendly refrigerant with zero ODP and GWP values. However, for associating fluids, available equations of state with high accuracy cannot correctly describe these different properties. In this work, new terms were developed specifically for this application.

The model we used is explicit in the Helmholtz energy, with independent variables of temperature and density. With the new associating terms, equations of state for these five fluids were developed based on experimental thermodynamic property data from the literature. The range of validity for temperatures, pressures, and densities of the equations of state for these three fluids were determined from the available data. The uncertainties in density, vapor pressure, saturated liquid and vapor densities, and caloric properties of the equations of state were also estimated from the available data. The unique behavior of thermodynamic properties for associating fluids was confirmed within the region of validity, and beyond the limits of validity during the procedure of fitting.