Determination of Third Virial Coefficients: A Mandatory Routine Test

C. G. Olivera-Fuentes
Department of Thermodynamics and Transport Phenomena, Simon Bolývar University, Caracas, Venezuela

C. M. Colina[C,S]
Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA, USA
colina@matse.psu.edu

The prediction of second virial coefficients, B, and their comparison with experimental values is a well-established, even mandatory test in the development of any equation of state (EOS). By contrast, a similar verification of third virial coefficients is much less common, partly because the experimental data are less widely available, but also because their more complex dependence on temperature makes them intrinsically more difficult to represent by analytical models. However, good prediction of B alone is not sufficient to guarantee the correct behavior of an EOS, even at low or moderate densities. In the present work, we show that third virial coefficients are also instrumental in predicting i.e. a correctly shaped Joule-Thomson inversion curve (JTIC) in the vicinity of the upper inversion temperature. We have previously shown that the shape of the JTIC of a fluid at supercritical conditions is shown to be directly related to its second and, specially, third virial coefficients. In this work, we show that the determination of third virial coefficients can be used to resolve, and actually avoid, conflicts among EOS presented in the literature. Examples are given for the importance of the determination of third virial coefficients for: a) multiparametric EOS, such as the Pitzer-Sterner EOS for CO_2, b) a molecular-based EOS, such as SAFT, and c) a cubic EOS such as Peng-Robinson.

Our results suggest that an analysis of third virial coefficients should be performed as a routine test of any, especially newly developed, EOS. If experimental data are not available for comparison, the present study suggests that molecular simulation results, molecular-based EOS, and/or generalized correlations, e.g., that by Orbey and Vera, may be relied on to supply the values needed to carry out such evaluations.