The Measurement of Vapor-Phase Composition, Vapor Density, and More with ^{1}H NMR Spectroscopy

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^{1}H NMR spectroscopy is rarely used for the analysis of vapor-phase mixtures. However, we have recently demonstrated that the composition of simple, vapor-phase mixtures can be determined with the same measurement uncertainty as for liquid-phase mixtures. For thermodynamic measurements such as vapor-liquid equilibria, it is also necessary to measure the vapor-phase density (or pressure) in addition to composition. We have devised a simple way to do this in the same experiment that is used to determine the composition. Specifically, a flame-sealed glass capillary that is filled with a reference fluid (e.g., methanol) is added to the sample tube. Then a density calibration is performed with a pure gas (e.g., methane) for which a high accuracy equation of state is available. A calibration curve is made from the signal area of the gas (from the NMR spectra) vs the density of the gas (from the EOS). The signal area for the gas is normalized by dividing by the signal area from the capillary, which accounts for any changes in pulse calibration, receiver gain, and the like. After calibration, the NMR tube + capillary pair can be used to determine the density of unknowns. The flame-sealed capillary can also serve other purposes. Importantly, we have found that it can be used to create a suspended liquid meniscus in the region of the sample tube that is otherwise filled with vapor. With this arrangement, it is possible to do a complete VLE measurement with a single NMR experiment. We have begun to explore different geometries and coatings for the capillary in order to optimize VLE measurements with this method.