New Frontiers in Mixture Vapor-Liquid Equilibria Measurement I: Can the Unconventional Become the Norm?

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Vapor-liquid equilibria (VLE) data, consisting of some combination of temperature, pressure, and liquid- and vapor-phase densities and compositions (T, p, ρ_L, ρ_V, x, y) of a two-phase system in thermodynamic equilibria, are the key data for modeling the thermodynamic properties of fluid mixtures. Such data have been measured on innumerable systems for more than a century. Yet, much of the data in the literature are characterized by large uncertainties and scatter within data sets and systematic differences between data sets. Clearly there is a need for better methods.

In this talk, we review the current state of VLE measurements and data and give an overview of several new (or, at least, not-commonly-applied) techniques for the measurement of VLE that offer the prospect of avoiding one or more of the systematic errors of classical techniques.

Densimetry can provide saturated liquid and/or vapor densities. Magnetic-suspension densimeters provide the most accurate measurements, and saturated liquid or vapor states are approached from the homogeneous phases using samples of well-known composition; thus, this can be considered a synthetic technique. Microwave cavity resonators measure the dielectric permittivity of a sample and detect dew and bubble points by an inflection in the permittivity as an isotherm or isochore is traversed; density is obtained via the Clasius-Mossotti relation (or variants for polar fluids). Advanced resonators can provide complete VLE information (T, p, ρ, x, y) by the solution of a set of simultaneous equations. Nuclear magnetic resonance (NMR) spectroscopy carries out a VLE experiment within a 5 mm diameter NMR "sample tube;" NMR in one sense "counts protons" (*i.e.*, hydrogen atoms in a molecule) and thereby determines the composition and density of the sample in situ; the temperature can be measured independently or by inserting a sealed capillary containing a temperature-sensitive NMR standard into the sample tube. Raman spectroscopy measures the inelastic scattering of monochromatic light off molecules, where the energy shift is due to vibrational modes, which can be used to uniquely identify molecules. For fluid mixtures, phase compositions can be quantified by comparing the intensity of spectral peaks for each component. Importantly, the measurement can be performed in situ, thus avoiding the complexity and uncertainty introduced by conventional sampling.

A common thread across these techniques is that they do not sample the phases for the determination of co-existing phase compositions but measure them in situ or rely on gravimetrically prepared mixtures. We will refer to other talks at the Symposium that describe these methods in greater detail.