Advantages of Accurate Dew-Point Data for the Determination of VLE

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Vapor-liquid equilibrium (VLE) data (*T*, *p*, *x*, *y*) are the most important data for fitting the parameters of mixture thermodynamic models, yet the literature data are generally characterized by large scatter within data sets and systematic differences between data sets. This situation hinders the further improvement of mixture models, and better experimental methods are clearly needed. Most traditional VLE experiments provide bubble-point data (*T*, *p*, *x*). In principle, a dew-point experiment (*T*, *p*, *y*) should provide equivalent information for defining the parameters of mixture models. In practice, it is difficult to test this hypothesis because fewer dew-point data are available in the literature, and they are often of lower accuracy.

Dew-point experiments offer advantages, including decreased sensitivity to volatile impurities (e.g., air), a smaller quantity of sample required, and lower uncertainty in the composition when working with gravimetrically prepared mixtures. The most notable disadvantage is the distorting effect of adsorption/precondensation; furthermore, the gravimetric preparation of gas-phase mixtures is difficult, especially for low-pressure mixtures.

Dew points can be measured in a variety of ways. The most common is the sampling of the vapor phase to determine composition in an experiment, where liquid and vapor phases are present in a measuring cell. One can also approach the dew point starting from the homogeneous vapor phase by either increasing the pressure along an isotherm or decreasing the temperature along an isochore. In this type of experiment a change in slope of some measurand indicates the dew point. This approach has been taken by numerous authors over the years, including the present authors and their coworkers, who have utilized densimetry and microwave-cavity techniques.

In this talk, we consider the general advantages and disadvantages of dew points and approaches for measuring them. We consider their utility in fitting mixture interaction parameters for six binary refrigerant blends measured along isotherms in a two-sinker densimeter.