B69 Phase Equilibria of Complex Fluid Mixtures: Modeling and Measurements With the Advanced Distillation Curve With Reflux (ADC-R)

Megan Harries, National Institute of Standards and Technology, 325 Broadway MS 647, Boulder, CO 80301; Marcia Huber, PhD, National Institute of Standards and Technology, 325 Broadway MS 647, Boulder, CO 80305; and Thomas J. Bruno, PhD, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305*

After attending this presentation, attendees will better understand how the vapor-liquid equilibrium of complex fluids (such as ignitable liquids) can be measured using a modified distillation apparatus and how such measurements may be used to interpret results of forensic headspace analysis.

This presentation will impact the forensic science community by providing a metrology to improve understanding of the complex, real-world fluids that those in this community encounter daily. The experimental approach presented may support forensic analysis conducted by headspace methods, including arson fire debris analysis, by providing quantitative, low uncertainty data describing the relationships between the vapor and condensed phases of a sample of interest.

Building on the successful development and widespread implementation of the ADC approach to measuring the volatility of complex fluids like fuels, the ADC-R metrology was developed to address the gap in our ability to experimentally determine the vapor-liquid equilibrium of fluids containing more than two components.[1] High-quality measurements of the volatility of pure components and binary mixtures are readily available, but the fluids encountered by a criminalist, like fuels, contain many more components.[2] For such complex mixtures, the ADC-R collects data about the chemical composition of both liquid and vapor phases across a variety of temperatures, elucidating the entire two-phase region at atmospheric pressure.

Two simple mixtures were used to demonstrate the ADC-R method: a decane + tetradecane binary mixture and the Huber-Bruno surrogate, a ternary mixture developed to represent the volatility of an aviation turbine kerosene.[1,3] These simple mixtures used to develop and test the approach were chosen because they are well understood, having been extensively measured in previous work. The experimental T-P-x-y data were compared to existing mixture models. For both test fluids, the measurements of vapor-liquid equilibrium were in very good agreement with model predictions. The data were also used to improve the binary interaction parameters used in modeling.

This study concludes that the ADC-R is an appropriate method for measuring the T-P-x-y behavior of the complex and polydisperse fluids used in the real world. Gasoline and other ignitable liquids relevant to the forensic community may be measured using ADC-R. This approach and the data it may make available in the future are relevant to the interpretation of forensic headspace analyses, for example, the carbon strip method conventionally used to analyze arson fire debris.[4]

Reference(s):

1. Bruno, T.J. Improvements in the Measurement of Distillation Curves. 1. A Composition-Explicit Approach. *Ind. Eng. Chem. Res.* 2006. 45: p. 4371-4380.
2. Outcalt, S.L. and B.-C. Lee. A Small-Volume Apparatus for the Measurement of Phase Equilibria. *J Res Natl Inst Stand Technol.* 2004. 109: p. 525-531.
3. Bruno, T.J., Huber, M.L. Evaluation of the Physicochemical Authenticity of Aviation Kerosene Surrogate Mixtures. Part II: Analysis and Prediction of Thermophysical Properties. *Energy & Fuels.* 2010. 24: p. 4277-4284.
4. Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal. 2016, ASTM International.

Chemical Analysis, Trace Evidence, Ignitable Liquids

*Presenting Author