Combination of Raman Spectroscopy and Gravimetry for the Investigation of Sorption Phenomena near the Dew Line of Fluid Mixtures

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Thermodynamic property models for fluid mixtures like empirical multi-parameter Helmholtz equations of state can describe the vapor-liquid phase behavior, however, the quality depends heavily on the underlying experimental data. For further improvements, particularly accurate measurements of dew-point densities are required. The state-of-the-art approach to accurately measure densities of gas mixtures is the application of a magnetic-suspension balance, which is based on the Archimedean (buoyancy) principle. Nevertheless, in the vicinity of the dew line, surface phenomena like sorption and capillary condensation can change the composition of the mixture under study and distort the measured density values, thus, increasing the uncertainty of the experimental data. Now, our goal is to observe the change of composition of the gas phase in parallel to the density measurement utilizing a non-invasive method to analyze the composition. For this purpose, Raman spectroscopy can be applied as it does not interfere with the gravimetric measurements. Against this background, we present the concept of a new measuring system, which combines gravimetric measurements using a magnetic-suspension balance and Raman spectroscopy to investigate sorption effects and capillary condensation near the dew line of binary gas mixtures. Beyond gaining a basic understanding of these surface phenomena in the context of accurate fluid-mixture densimetry (i.e., sorption on non-porous media), the new measuring system will also enable targeted investigations of surface phenomena on porous media, e.g., ionogels (ionic liquid + aerogel) near dew-point conditions. Since the composition of the gas phase is monitored as material is adsorbed onto the surface, this kind of experiment will shed light on gas separation and purification processes, which is a fundamental contribution to solvation science. As a proof of concept, we show recent results of spectroscopic measurements near the dew line of CO_2 + C_3H_8 mixtures using a compact Raman backscattering setup.