Molecular Dynamics Meets Gravimetry: Progress in Highly Accurate Dew-Point Density Measurements

Markus Sekulla[1, S], Luca Bernardini[1], Maximilian Kohns[2] and Markus Richter[1, C]

[1]*Applied Thermodynamics, Chemnitz University of Technology, Chemnitz, Germany*
[2]*Laboratory of Engineering Thermodynamics, RPTU Kaiserslautern, Kaiserslautern, Germany*
m.richter@mb.tu-chemnitz.de

The role of phase equilibria in fluid mixtures is pivotal in numerous industrial applications and, thus, forms a central aspect of thermodynamic fluid property research. More accurate measurement data are crucial for developing and refining fluid mixture models. Nowadays, gravimetric density measurement apparatuses employing magnetic suspension balances provide highly accurate density measurements. However, surface effects like adsorption affect measured densities, especially near the dew line. While methods using multiple sinkers have been developed to mitigate the adsorption effect, even measurements employing these methods can be improved by considering accurate information about the adsorbate structure on the sinker surfaces. Furthermore, many densimeters in use today do not account for adsorption effects, leading to significant uncertainties in measurement data due to insufficient knowledge about the adsorbate. To reduce this uncertainty, we investigated the experimentally observed adsorption using molecular dynamics simulations. The simulated adsorption isotherms of CO_2 and lower alkanes were validated against experimental adsorption data measured with instruments accounting for the adsorption effect. In the validation, the surface topographies of the actual sinker surface were considered, as assessed by atomic force microscopy and a confocal Raman microscopy. Our simulation-based approach allowed for determining the density of the adsorbed phase and comparing it to assumptions found in the literature [1-3]. We discovered that the widely used constant adsorbate density does not hold, as we observed significant changes in the adsorbate structure along the adsorption isotherm. Based on these findings, we present a novel method for determining the density of the adsorbed phase on the sinker surfaces.

References

1. *Yang, X.; Richter, M. (2020)*. Experimental Investigation of Surface Phenomena on Quasi Nonporous and Porous Materials Near Dew Points of Pure Fluids and Their Mixtures. Ind. Eng. Chem. Res. *59*, 3238-3251
2. *Moellmer, J.; Moeller, A.; Dreisbach, F.; Glaeser, R.; Staudt, R. (2010)*. High-pressure adsorption of hydrogen, nitrogen, carbon dioxide, and methane on the metal–organic framework HKUST-1. Microporous and Mesoporous Materials. *138 (1-3)*, 140-148
3. *Cavenati, S.; Grande, C. A.; Rodrigues, A. (2004)*. Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures. J. Chem. Eng. Data. *49 (4),* 1095-1101