Evaluation of the Applicability and Limits of Dynamic Light Scattering (DLS) for the Simultaneous Measurement of Diffusivities

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Dynamic light scattering (DLS) is a powerful and well established technique for the determination of transport and further thermophysical properties of pure fluids and fluid mixtures. In comparison to conventional techniques making use of macroscopic gradients, the working principle of DLS in macroscopic thermodynamic equilibrium is particularly useful for the determination of Fick and thermal diffusivities close to or within the two-phase region. Experimental and theoretical work, however, show also limitations of the DLS technique in the near-critical region. Here, only one hydrodynamic mode may be observable and an unambiguous classification of DLS signals in connection with mutual and thermal diffusivity is not possible in all cases. In general, the capabilities and limitations of DLS for the simultaneous determination of Fick and thermal diffusivities in binary mixture have not been examined yet.

The present contribution evaluates the accessibility of diffusivities in binary mixtures consisting of carbon dioxide, methane, and propane by DLS. Heterodyne DLS experiments and theoretical calculations of the Rayleigh ratio were performed at 125 different thermodynamic states for an equimolar methane–propane model mixture across the two-phase region including the gas, liquid, supercritical, and the two-phase region. The signals obtained in the DLS experiments could be attributed to the thermal, mutual, a mixed, or an effective diffusivity. The classification was performed with the help of experimental and calculated Rayleigh ratios as well as temperature-, pressure-, and concentration-dependent trends of the named diffusivities. Which diffusivities are accessible is strongly related to the location of the investigated thermodynamic state point relative to the phase envelope of the mixture. The developed classification strategy which can be applied to arbitrary binary fluid mixtures, was tested for further 170 thermodynamic state points of binary mixtures consisting of carbon dioxide, methane, and propane over a wide range of temperatures, pressures, and molar fractions.