

# Diffusion and Thermodiffusion of CO<sub>2</sub> Mixtures at the Extended Critical Region

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Supercritical carbon dioxide (CO<sub>2</sub>) mixtures play a vital role in various environmental, power, and chemical industry applications. While the thermophysical properties of CO<sub>2</sub> and certain binary mixtures are well-documented, there is a notable lack of comprehensive knowledge with respect to their transport properties. This gap is particularly evident in the extended critical region, where the presence of anomalous behavior of these properties was highlighted by experimental and molecular simulation studies<sup>1,2</sup>.

Molecular modeling and simulation is a powerful tool for predicting dynamic properties of fluids and for understanding the microscopic interactions governing diffusion and thermodiffusion. In this work, we report molecular simulation-based findings on diffusion and thermodiffusion of binary supercritical CO<sub>2</sub> mixtures with hydrogen, methane, ethane, isobutane, benzene, toluene and naphthalene near the infinite dilution limit. These investigations encompass the temperature range between 290 and 340 K along the 9 MPa isobar and three solute mole fractions (0.5, 1.0 and 1.5 mol%).

As a second-order effect, the mass flux induced by the Soret effect is relatively small and therefore challenging to evaluate with equilibrium molecular dynamics simulation. Nonetheless, this technique allows for the determination of the different contributions to the thermal diffusion coefficient, and thus to the understanding of the associated microscopic mechanisms. Further, because of pronounced density fluctuations in the extended critical region, molecular dynamics simulations are particularly challenging and require extensive sampling and rather large system sizes.

It was found that slight variations of temperature and pressure within the extended critical region can lead to drastic changes in these mixtures, like a 50% reduction of density, a twofold increase of shear viscosity, and a notable surge of diffusion coefficients. This peculiar behavior, both for thermodynamic and transport properties, is most pronounced in the vicinity of the so-called Widom line. The substantial composition sensitivity of the Fick diffusion coefficient in the extended critical region can be attributed to significant changes of the thermodynamic factor. This factor typically exhibits a pronounced minimum near the Widom line, even with only 0.5 mol% of solute. This minimum corresponds to density fluctuations and clustering effects in the extended critical region. Furthermore, molecular simulation data reveal a clear breakdown of the Stokes-Einstein relation, indicating a decoupling of diffusivity and viscosity around the Widom line, which marks the transition from a high-density to a low-density fluid.

The Soret coefficient  $S^T$  relates the thermal diffusion coefficient  $D^T$  to the Fick diffusion coefficient  $D_{ij}$ ,  $S^T = D^T/D_{ij}$ . As a result, it is expected that  $S^T$  exhibits an anomalous behavior in the near-critical region, mirroring effects observed for the Fick diffusion coefficient. This assumption is substantiated by findings for three CO<sub>2</sub> mixtures, indicating that the Soret coefficient has an extremum close to the Widom line. However, an in-depth examination of the various constituents contributing to the thermal diffusion coefficient  $D^T$  pinpoints the enthalpic term, and not the thermodynamic factor, as the primary factor. Consequently, for precise Soret coefficient calculations with equilibrium methods, a meticulous evaluation of the partial molar enthalpies is indispensable.

## References

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