Diffusion of hydrocarbons diluted in supercritical carbon dioxide mixtures

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Diffusion crucially affects chemical engineering processes, such as distillation, absorption or extraction. Besides experimental techniques, molecular modeling and simulation is a powerful tool for the prediction of fluid properties as well as the analysis of molecular interactions that lead to diffusion.
Here, we present the results of a molecular simulation study on diffusion of seven binary supercritical carbon dioxide ($scCO_2$) mixtures with hydrogen, methane, ethane, isobutane, benzene, toluene and naphthalene along the 9 and 10 MPa isobars in the temperature range between 290 and 340 K. Because of pronounced density fluctuations in the extended critical region, molecular dynamics simulations are particularly challenging and require extensive sampling and large system sizes. However, it has been shown in previous work [1,2,3] that simple, rigid, non-polarizable molecular models are able to accurately predict transport properties of pure fluids, binary, ternary and quaternary mixtures of non-polar to hydrogen-bonding species.
Slight variations of temperature and pressure in the extended critical region may cause the density of these mixtures to halve, the shear viscosity to double and the self-diffusion coefficient to rise strongly. This anomalous behavior of thermodynamic and transport properties is pronounced near the so Widom temperature. Further, it is also shown that the thermodynamic factor has a minimum around that temperature. Just a few mole percent of a solute in $scCO_2$ can cause the thermodynamic factor to approach values of zero and thus strongly affect the Fick diffusion coefficient. Fig. 1 shows that the Fick diffusion coefficient has a clear dependence on the molecular mass and self-diffusion coefficient of pure CO_2 in the $scCO_2$ mixture. The goal is to present an equation to predict the diffusion coefficients based on the properties of pure $scCO_2$ and the molecular mass of the solute and density of $scCO_2$ mixtures.

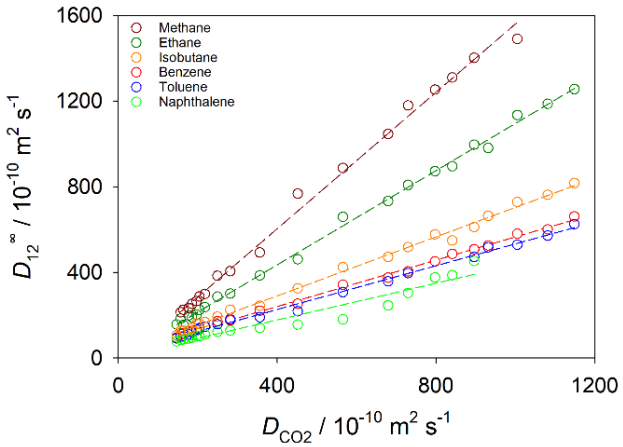

Figure 1: Dependence of the infinite dilution Fick diffusion coefficient on the self-diffusion coefficient of pure CO_2 for diluted methane, ethane, isobutane, benzene, toluene and naphthalene in scCO2. Bullets represent molecular simulation data along the 9 MPa isobar and temperatures between 290 K and 345 K.

References

[1] G. Guevara-Carrion, T. Janzen, Y. M. Muñoz-Muñoz and J. Vrabec: *Mutual diffusion of binary liquid mixtures containing methanol, ethanol, acetone, benzene, cyclohexane, toluene and carbon tetrachloride*. J. Chem. Phys. **144**, 124501 (2016).

[2] G. Guevara-Carrion, T. Janzen, Y. Gaponenko, A. Mialdun, T. Janzen, V. Shetsova and J. Vrabec: *Interplay of structure and diffusion in ternary liquid mixtures of benzene + acetone + varying alcohols*. J. Chem. Phys. **149**, 064504 (2018).

[3] G. Guevara-Carrion, R. Fingerhut and J. Vrabec: *Fick Diffusion Coefficient Matrix of a Quaternary Liquid Mixture by Molecular Dynamics*. J. Phys. Chem. B 124, 4527-4535 (2020).