The thermodynamic factor: The key to understand complex diffusion behavior in fluid mixtures

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Separation processes in chemical engineering, such as distillation, absorption or extraction, are affected by diffusion. In recent years, molecular modelling and simulation has become an alternative tool not only to accurately predict dynamic properties of fluids, but also to interpret experimental data because it offers access to microscopic details which are often inaccessible with experimental techniques. In preceding work of our group [1,2,3], it was shown that transport properties of pure fluids, binary and ternary mixtures of non-polar, polar and hydrogen-bonding species can be accurately predicted with simple, non-polarizable molecular models.

We present the results of a molecular simulation study of fluid mixtures, where complex diffusion behavior has experimentally been found and offer an explanation based on the hydrodynamic and thermodynamic components of the Fick diffusion coefficient. Special attention is paid to mixtures near critical and demixing regions, where in many cases strong discrepancies between different measurements of the Fick diffusion coefficients are found. Also molecular simulations are challenging in these regions and require extensive sampling due the presence of pronounced density fluctuations.

In molecular dynamics simulations, the Fick diffusion coefficient is typically calculated from the Maxwell-Stefan diffusion coefficient and the derivative of the chemical potential in form of the thermodynamic factor. Because the chemical potential cannot be measured by experiment, this factor is usually estimated from vapor-liquid equilibrium or excess enthalpy data, employing an equation of state or an excess Gibbs energy model. Nevertheless, it can also be sampled by molecular simulations, as it was done in this work.

Near the infinite dilution limit, the thermodynamic factor is usually assumed to be unity and to have an insignificant influence on the value of the Fick diffusion coefficient. However, under certain conditions, even for solvent concentrations of a few mole percent only, the thermodynamic factor may approach values of zero, having a major impact on the Fick diffusion coefficient. For example, the thermodynamic factor of a 1 mole% mixture of benzene in carbon dioxide may reach values around 0.5 in the near-critical region. Thus, the anomalous behavior of diffusion found experimentally in this region for this mixture and the strong composition dependence of the Fick diffusion coefficient can be rationalized, if the thermodynamic factor is taken into account.

Furthermore, for highly non-ideal mixtures and those approaching a demixing region, the contribution of the thermodynamic factor to the observed Fick diffusion coefficient may become much more important than the hydrodynamic contribution given by the Maxwell-Stefan diffusion coefficient

References

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