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Fick and Maxwell-Stefan diffusion in quaternary liquid mixtures by molecular simulation

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Most mass transfer processes occurring in biological or chemical engineering involve multicomponent liquids. However, diffusion coefficients have experimentally been measured only for a few ternary or higher order mixtures because of challenges related to the description of multicomponent diffusion processes. In recent years, molecular modelling and simulation has become an alternative tool not only to accurately predict dynamic properties of liquid mixtures, but also to interpret experimental data.

With molecular dynamics simulations, the Fick diffusion coefficient is typically calculated from the Maxwell-Stefan diffusion coefficient and the mole fraction derivative of the chemical potential in the form of the thermodynamic factor. Since the chemical potential cannot be measured directly by experiment, this factor is usually estimated from vapor-liquid equilibrium or excess enthalpy data. However, it can be sampled by molecular simulations employing Kirkwood-Buff integration (KBI), as it is done in this work.

We present the results of a molecular simulation study of the quaternary mixture water + methanol + ethanol + 2-propanol, where complex diffusion behavior is expected because of the ubiquitous presence of hydrogen bonding. In preceding work of our group [1,2], it was shown that the diffusion coefficients of the pure liquids, all aqueous binary subsystems and the ternary subsystem water + methanol + ethanol mixture can be accurately predicted with simple, non-polarizable molecular models. Further, the performance of the KBI approach to sample the thermodynamic factor was recently thoroughly addressed [3] and implemented for quaternary mixtures. Therefore, we expect that the present predictions of the Fick diffusion coefficient matrix of the quaternary mixture under study will be close to that of the real system.

The influence of the reference frame on the Fick diffusion coefficient matrix of the quaternary mixture and its ternary subsystems was also analyzed. It was found that the main elements of the diffusion matrix exhibit a weaker dependence on the reference frame than the cross elements. As expected, the ternary mixture consisting solely of alcohols shows smaller variations among different reference frames. The main elements of the diffusion matrix of the aqueous mixtures show stronger variation when the reference frame is varied, which can in part be explained by the relatively large differences between the partial molar volume of water and its pure substance volume.

References

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