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Simplified theory to predict mixture diffusion in zeolites: Accounting for strong correlations and examining the role of adsorption thermodynamics

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The Maxwell–Stefan (MS) equations have been extensively used to describe mixture diffusion in zeolites. Correlation effects can arise due to molecules unsuccessfully attempting to pass each other in the very narrow pores of the zeolite, e.g., at high loadings of adsorbed molecules. In an extreme situation, diffusion may even become anomalous, giving rise to a single-file phenomenon. These correlation effects are captured in the so-called "exchange terms" within the framework of the MS equations. The exchange terms are often calculated from pure component data using empirical approaches with different fits for different combinations of zeolite hosts and molecules. These computations, in turn, can be fairly tedious, especially for large multicomponent systems. It is therefore advantageous to be able to use a simplified theory to capture the effect of strong correlations. To this end, the MS equations are simplified to predict mixture diffusion behavior in the case of strong correlation effects. Intermolecular exchange coefficients are not required. No empirical relations are employed. This simplified model is used to predict the diffusion behavior in the separation of a CH_4-C_3H_8 mixture through a silicalite membrane [1].

Diffusion in zeolites is also closely coupled with adsorption due to the tightly confining pore space in the zeolite where the concept of a bulk fluid phase ceases to exist. Adsorption effects are accounted for in the MS theory through the mixture thermodynamic correction factors, which are derived using the pure component adsorption isotherms and theories such as the Ideal Adsorbed Solution Theory (IAST). The calculation of mixture thermodynamic correction factors in the MS equations can also pose a computational hurdle especially for large systems, and if theories such as the IAST have to be employed. It is expected that, if a vacant adsorption site is available, the adsorption of a species inside the zeolite pore should be dictated by the pure component adsorption isotherm alone, and that mixture adsorption thermodynamics should not play a role, or else correlation effects should be present in adsorption as well, in which case theories such as the IAST cannot be used. To this end, the MS equations are simplified to employ only the pure component thermodynamic correction factors. This simplified model was used to predict mixture diffusion for two cases of practical interest [1]: (i) the separation of a N_2-CH_4 mixture through a SAPO-34 membrane, and (ii) the alkylation of C_6H_6 with C_2H_4 over H-ZSM-5. In all cases, predictions from the simplified models are favorably compared to results from the more complex MS equations or experiments, indicating that the simplified models can serve as good starting approximations, and can also speed up mixture diffusion calculations in zeolites.

References

[1] S. Rao, M.-O. Coppens: *Predicting mixture diffusion in zeolites: Accounting for strong correlations with a simplified theory and examining the role of adsorption thermodynamics.* Journal of Physical Chemistry C **116**, 26816–26821 (2012)