Mapping Non-Ideal Contributions to Gas Solubility in Multicomponent Aqueous-Organic Systems

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Multicomponent alkanolamine + water solutions are commonly associated with liquid-phase regenerative carbon dioxide separation, including natural gas sweetening and post-combustion carbon capture. However, regeneration of amine solutions comes with a significant energy penalty. Hydrated polyamine facilitated transport membranes aim to improve separation efficiency through gas-to-gas separation by leveraging a similar aqueous amine chemical environment. For separation processes involving either alkanolamine solutions or hydrated polymers, inert species are of great importance: natural gas sweetening aims to minimize hydrocarbon loss from the regenerative process, while post combustion separation performance relies critically on the relative solubility of nitrogen and carbon dioxide species. However, reliable solubility data for multicomponent systems is scarce, and in the case of hydrated polymers represents a significant experimental challenge. To investigate solubility in these complex aqueous-organic systems, we utilize molecular dynamics with a replica-exchange accelerated multistate Bennet acceptance ratio method. This allows estimation of solvation free energies for inert gas species across a range of compositions and temperatures, while overcoming slow degrees of freedom in dry alkanolamine or polymeric systems. For methane solubility in methyldiethanol + water, our results are in excellent agreement with reference experimental studies, and allow parametrization of temperature-correlated Redlich-Kister and Morgules equations providing an analytical map of solubility for the system. We confirm the existence of a strongly temperature-dependent non-ideal contribution to methane solubility, likely caused by clustering of methyldiethanol in solution. By extending the method to hydrated polymer systems, we show how the dependence of solubility on water content and temperature can be estimated directly from molecular methods for systems where difficulty of measurement or material synthesis limits accessibility to experimental data.