

Transferable Potentials for Mixed Alcohol-Amine Interactions

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A subtle problem arises when characterizing site-site potentials for molecules like primary alcohols, but it may not express itself until the potentials are applied to mixtures. For example, consider the disperse attraction energy between the CH₂ and OH sites in a united atom model (UAM) of primary alkanols. This parameter would typically be estimated by something like $E_{ij} = \sqrt{E_{ii}E_{jj}}(1-K_{ij})$, where E_{ij} is the depth of the potential well between sites i and j , and K_{ij} is an adjustable parameter. In most cases, K_{ij} is neglected during characterization of the pure component potentials. Unfortunately, the accuracy of phase equilibrium predictions with that approach is less than quantitative, necessitating application of K_{ij} , or something similar. Unfortunately, phase equilibria exist at the molecule-molecule level, but the UAM does not pertain to that level. The UAM applies to site-site interactions. That is, a non-zero K_{ij} between a CH₂ site on octane and an OH site on butanol, must also apply to the interaction between a CH₂ site on butanol and an OH site on butanol if the UAM is to be applied self-consistently. The mixture interactions are more sensitive to assumptions about K_{ij} because the sites are not bound as in a pure fluid so there is no coupled interaction that would automatically be altered to cancel the error in that assumption, as occurs in regressing potentials for pure fluids. When optimizing the pure fluid, the mixed site attractive interaction is confounded with other contributions to the UAM.

In this study, we address this confounded interaction problem by successively optimizing the site-site interactions while accounting for mixture observations as well as pure fluid vapor pressure and density. This successive approach is greatly facilitated by the perturbative approach of the Step Potentials for Equilibria And Discontinuous Molecular Dynamics (SPEADMD) model. Because the attractive interactions can be treated as perturbations, both for the mixtures and the pure fluids, trial potentials can be rapidly evaluated without repeating the molecular simulations. Estimates for K_{ij} of CH₂-OH and CH₂-NH₂ are developed for mixtures of n-alkanes with alcohols and amines.

A related problem develops when treating hydrogen bonding interactions. In molecular models based on explicit treatment of hydrogen bonding interactions, like the SAFT model, SPEADMD, and older versions of the CHARMM potential, it is necessary to approximate the solvation energy in a manner similar to the disperse interaction energy. Typically, it is assumed that $U_{ij} = (1-H_{ij})(U_{ii} + U_{jj})/2$, where U_{ij} is the hydrogen bonding energy and H_{ij} is the empirical correction factor. The fallacy of neglecting H_{ij} is demonstrated by treating mixtures of alcohols with amines, for which H_{ij} is significantly less than zero. The need for a non-zero value of H_{ij} shows up in phase behavior, heats of mixing, and in the spectroscopic studies that form the basis of the Kamelet-Taft parameters. In molecular models where hydrogen bonding interactions are implicit, like point charge models, anomalous solvation energies cannot be directly addressed. For amine-alcohol mixtures, this defect shows up as a large sign error in the predicted heat of mixing. In the present work, estimates of H_{ij} for OH-NH₂ interactions are presented for mixtures of alcohols and amines.