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Transferable potentials for mixed alcohol–amine interactions

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Abstract

Transferable potentials for the hydrogen bonding interactions of alcohols with amines are characterized. These systems exhibit anomalously strong solvation interactions that make the formalism of discontinuous potentials (the SPEADMD model) especially advantageous relative to point charge potential models. Exothermic heats of mixing are observed along with activity coefficients less than unity. A database of 11 amines and 6 alcohols is analyzed with 27 binary mixtures to train and validate the solvation interactions. Comparisons are made to the Peng–Robinson and Peng–Robinson–Wong–Sandler models. The SPEADMD model provides accuracy of roughly 3% overall when corrected for vapor pressure deviations. Transferable site–site parameters for disperse interactions are not treated in the present work, but the outline of such a completely predictive model is described.

Keywords: Molecular simulation; Hydrogen bonding; Solvation; Vapor–liquid equilibria; Amines; Alcohols; Transferable potentials; Vapor pressure; Double azeotrope

1. Introduction

Molecular simulation is steadily developing into a practical tool for engineering correlation and prediction [1]. This approach breaks the molecular interactions down into individual site–site "force fields," based on which Newton's laws of motion can be applied to simulate the properties of macroscopic fluids based on the detailed dynamics of relatively few molecules (typically ∼100). Note that it is also possible to achieve equivalent results for the thermodynamic properties when applying Monte Carlo methods to simulate the detailed configurations of the molecules. The key to successful molecular simulation is to characterize site–site interactions that can be "transferred" from one molecule to another. For example, the CH_2–CH_2 interactions between the middle sites in *n*-pentane should accurately approximate the CH_2–CH_2 interactions between the middle sites in *n*-pentadecane. The breadth of applicability and accuracy of molecular simulation breaks down when this kind of transferability breaks down.

The development of transferable force fields took a major step forward with the development of the transferable potentials for phase equilibria (TraPPE) model. Siepmann and coworkers realized that vapor pressure was a key property for engineering applications, exhibiting high sensitivity to the details of the potential while laying the foundation for practical applications of phase equilibria of both pure fluids and mixtures. Their work is based most broadly on the Lennard–Jones united atom model and provides accuracy of roughly 60% absolute average deviation (%AAD) for vapor pressure and 2%AAD for liquid density over a temperature range of $T/T_c = [0.9, 0.6]$, where T_c is the critical temperature in Kelvins. A united atom model makes the assumption that hydrogen atoms can be subsumed with their bound carbons to form an single effective potential representative of each carbon atom and all its bound hydrogens. More recent developments of transferable potentials are the anisotropic united atom (AUA) model of Fuchs and coworkers [2] and the SPEADMD model that is the focus of the present work [3,4]. The AUA model also applies Lennard–Jones potentials, but allows the centers of the potential to vary from the center of the carbon nucleus, based on the idea that the hydrogen atoms shift the center of force of the united atom potential. The AUA model typically provides accuracy of 25%AAD for vapor pressure and 2% for liquid density over a temperature range of $T/T_c = [0.9, 0.6]$. The SPEADMD model applies united atom potentials centered on the large atom, but adopts a discretized description of the potential in the form of step potentials. The

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adaptation of step potentials is based on the assumption that sites in the middle of a molecule lack the spherical symmetry that formed the basis for the development of the Lennard–Jones potential and thus the optimal description of site–site potentials should be reconsidered from the ground up. The SPEADMD model typically provides accuracy of 15% AAD in vapor pressure and 4% on liquid density over a temperature range of $T/T_c = [0.9, 0.45]$. Note that the largest deviations in vapour pressure prediction tend to occur at the lowest reduced temperatures, so it is important to consider the temperature range when comparing potential models.

The development of transferable potentials for hydrogen bonding components presents a more substantial challenge, relative to components that can be accurately characterized simply with disperse interactions. The typical approach with models like the TraPPE or AUA models is to add point charges distributed around the molecule to mimic the surface charge distribution determined quantum mechanically. Often, the distribution of point charges to achieve reasonably accurate surface charge distributions is not unique. The issue is then to select a charge distribution that permits accurate characterization of the vapor pressure and density for the same site type in multiple molecules. For example, the charge distribution around the hydroxyl group in alcohols should be transferable to multiple alcohols. Generally, adding point charges tends to make the simulation run more slowly. The SPEADMD model characterizes hydrogen bonding in terms of stereospecific, short-range potentials. This approach to hydrogen bonding potentials is compatible with Wertheim's theory [5,6]. In the SPEADMD model, the interactions between various sites are specifically tabulated in advance of the simulation. Adding hydrogen bonding sites slows the simulation, but the advantage of Wertheim's theory is that it is sufficiently accurate to apply without simulation of the full potential (i.e. including the hydrogen bonding sites). In most cases, only the reference potential need be simulated and the impact of the hydrogen bonding potentials can be inferred.

A special challenge is encountered in the case of alcohol–amine interactions. Similar to the Lorentz–Berthelot combining rule for disperse interactions, a guideline exists for the solvation energy of hydrogen bonding interactions. (In hydrogen bonding jargon, solvation refers to interactions between unlike molecules and association refers to interactions between like molecules.) The guideline is that $h_{ij}^{\mathrm{AD}} = 0$ for the following relation:

$$\varepsilon_{ij}^{\mathrm{AD}} = 0.5(\varepsilon_{ij}^{\mathrm{AD}} + \varepsilon_{ij}^{\mathrm{AD}})(1 - h_{ij}^{\mathrm{AD}}) \tag{1}$$

where $\varepsilon_{ij}^{\mathrm{AD}}$ is the solvation energy between a proton acceptor on the *i*th site and a donor on the *j*th site. A similar relation holds for $\varepsilon_{ij}^{\mathrm{DA}}$. In mixtures of alcohols with alcohols, aldehydes, or thiols, Eq. (1) with $h_{ij}^{\mathrm{AD}} = 0$ gives reasonable results. Eq. (1) also works for mixtures of hydrogen bonding species with hydrocarbons, since the number of bonding sites is set to zero for the hydrocarbons. Mixtures of alcohols with amines require large negative values of h_{ij}^{AD} to accurately characterize the data, however. This indicates synergistic bonding interactions that are more strongly favorable than expected by the general guideline. An alternative approach is to correlate the data for these systems with large negative values of the binary interaction parameter for disperse interactions, k_{ij} [7]. In our opinion, such an approach undermines development of transferable characterizations of the energetic interactions.

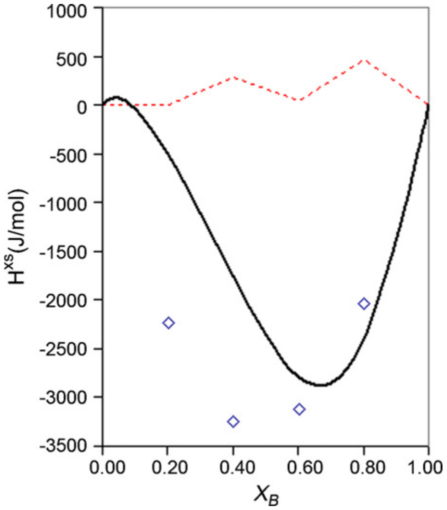

Fig. 1. Excess enthalpy of *n*-butylamine(1) + water(2) at 25 °C as predicted by (- - -) a point charge model [8] and by the SPEADMD model (—). Points represent experimental data [1].

This perspective is straightforward to characterize within the context of Wertheim's theory, but there is no guideline for point charge models that is comparable to Eq. (1). The solvation interactions of point charge models are implied by the point charge distribution. Since the point charges are assigned based only on surface charge distributions or, at most, based on pure component vapor pressure data, it is highly unlikely that the synergy of the binary combination would be recognized. This limitation is apparent in predictions of heats of mixing by point charge models for the butylamine + water system. As illustrated in Fig. 1, the point charge models predict endothermic mixing, whereas the experimental data exhibit exothermic mixing [1]. The results of SPEADMD are a prediction in the sense that the mixture parameters were determined from VLE, not the heat of mixing.

In this context, we pursue SPEADMD transferable potential models for alcohol–amine interactions in the present work. In particular, the present work focuses on transferably characterizing the solvation interactions, with characterization of transferable mixed site–site interactions to come at a later date. Section 2 further clarifies the background of the SPEADMD model and the basis of the mixture correlations. Section 3 summarizes the database for the present study and the results for vapor–liquid equilibria (VLE) correlations. The final section summarizes conclusions.

2. Background on the SPEADMD model

The SPEADMD model has its origins in work by Hu and Elliott and Cui and Elliott. Those works showed that simulated