Relevance of the thermodynamic ERAS model for liquid mixtures with components exhibiting a small degree of self-association

Christopher G. Jesudason, Ching Koon Yau

http://dx.doi.org/10.1016/j.molliq.2017.02.120

Highlights

- ERAS model of thermodynamics is analyzed for consistency.
- Quantum DFT calculations are invoked in place of set parameter tables.
- Model consistently extended to deal with weakly-associating molecules.
- Extended treatment tested against COSMO-RS.
- Results of optimizations yield physically reasonable values of ERAS parameters.

Abstract

The thermodynamic extended real associated solution (ERAS) model is reviewed and modified to accommodate weakly associating components. ERAS is a theoretical scheme applied to binary liquid mixtures whereby certain physically meaningful parameters such as the association equilibrium constants, species reduced volume and energy terms may be determined by optimization against the experimental excess molar volumes and enthalpies. The implicit assumption used for any non-associating molecule B is to routinely set the hydrogen-bonding energy $\Delta h_B^*$, reaction volume $\Delta v_B^*$ and association constants $K_B$ to zero. It is proven here that such assignments lead to singularities in the ERAS parameters that are featured in the excess state functions used. A series of optimizations using the results of conductor-like screening model for real solvents (COSMO-RS) on the excess enthalpy $\Delta h^*$ of dimethoxymethane in binary mixtures with a series of alcohols are determined, and the parameters $\Delta h_B^*$, $\Delta v_B^*$ (mixed enthalpy of reaction) and $X_{AB}$ (interaction parameter) are determined. It is shown that the stipulated range of $X_{AB}$ values from ERAS theory requires minor modification if the above assumptions are not made. The magnitude of the computed variables are shown to be physically reasonable. The Bondi group averaged estimates for $s_i$, the ratio of the van der Waals (vdW) surface area to the vDW volume for molecule $i$, are contrasted against the more specific and reliable derivations from quantum calculations when calculating the excess functions. The degree of correlation is improved using the latter $s_i$ values. We conclude that the results of the optimizations indicate that the ERAS model can be extended even to weakly self-associating components previously considered impossible in especially engineering thermodynamical applications, with the above modifications and refinements.

Keywords

Extended real associated solution model; COSMO conductor-like screening model; DFT QM calculations; Dimethoxymethane; Excess enthalpy; Excess Gibbs energy
Relevance of the thermodynamic ERAS model for liquid mixtures with components exhibiting a small degree of self-association
Relevance of the thermodynamic ERAS model for liquid mixtures with components exhibiting a small degree of self-association