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Correlation of vapor-liquid equilibrium data of amines in organic and aqueous mixtures with the F-SAC model

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Aqueous and organic mixtures containing amines are present in several industrial applications. For instance, in acid corrosion control of crude oil refineries by means of blended amines and ammonia solutions. In post-combustion carbon dioxide (CO₂) capture plants, the absorbent solvent contains amines to further increase CO₂ absorption. In order to project, simulate and optimize these processes, thermodynamic models are fundamental. In this work, parameters for the Functional-Segment Activity Coefficient (F-SAC) model were estimated from vapor-liquid equilibrium (VLE) data. In comparison with state-of-the-art group contribution model UNIFAC (Do), F-SAC has less parameters subject to optimization, which makes functional groups introduction easier and less experimental data dependent.

The F-SAC model fits into the category of group contribution method models. This approach considers a molecule to be a collection of functional groups. Although the number of existing molecules is virtually infinity, they consist of a smaller number of functional groups. Therefore, such a model is of interest as it can predict properties of mixtures for which experimental data is not yet available. In order to describe amines in the F-SAC model, five functional groups were introduced. A division among primary, secondary and aromatic amines was proposed, with exclusive groups for methylamine and dimethylamine. This was found to be the best solution available by a trial and error iterative process of group assignment and parameter estimation. With regard to physical properties of the considered mixtures, amines appear to strongly interact with water, presenting negative deviations from an ideal solution. This phenomenon indicates hydrogen bonds are involved. So as to account for that, each amine functional group has a proton acceptor site, corresponding to the nitrogen lone pair of electrons. On the other hand, mixtures of amines with hydrocarbon compounds show positive deviations from ideality. This is because hydrocarbons are apolar and amines are polar compounds, which was confirmed by the estimated model parameters.

Parameter estimation was carried out with a local search algorithm, considering an objective function which minimizes the sum of squared relative errors in bubble point pressures for all experimental points considered. The experimental dataset was collected from literature and is currently stored in form of a text file database. The parameter estimation procedure required initial values for all parameters being estimated. As in the F-SAC model parameters are electrostatic or surface areas, this information was easily retrieved from *ab initio* calculations with the COSMO (COnductor-like Screening MOdel) theory. After a solution for the parameter estimation problem was found, the F-SAC model was able to correlate all 2617 VLE experimental data points with 2.76 % average relative error and within 13.11 % maximum deviation. For the sake of comparison, UNIFAC (Do) model response for the same experimental dataset with literature parameters is 6.35 %, maximum error of 77 % . The F-SAC model better described alkanolamine solutions, which are a known deficiency of UNIFAC (Do) due to multiple functional groups appearing in the same molecule.

Results obtained confirm potential development for COSMO based models. As the F-SAC model requires less parameters, functional groups introduction and reparametrization demand less computational and experimental resources. Future F-SAC model extensions may rely on the general discussion presented in this work and include other nitrogenated compounds not currently assigned.