

PHASE EQUILBRIA FOR BIO-DERIVED CHEMICALS

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Michigan State University is actively pursuing reactive distillation for economical upgrading of bio-derived platform molecules to chemicals. To support the process design and scale-up, thermodynamic properties are measured and estimated. A P-x-y apparatus has been developed to collect binary VLE data for the multicomponent systems involved in reactive distillation for production of ethyl lactate, triethyl citrate, and diethyl succinate. The apparatus is capable of measuring VLE and VLLE at temperatures between 25°C and 80°C and pressures down to 0.7 kPa. Data pass either the area or point-to-point thermodynamic consistency tests. Systems measured include ethanol + ethyl lactate, water + ethyl lactate (maximum pressure azeotrope), ethanol + triethyl citrate, water + triethyl citrate (VLLE), ethanol + diethyl succinate. The use of the P-x-y method permits measurements of reactive systems at low temperature where insignificant reaction occurs. A T-x-y apparatus has been used to collect data for lactic acid + water, as well as selected multicomponent systems.

Lactic acid + water is a complex solution due to the presence of oligomers. The oligomers are ester chains formed between the carboxylic acid and alcohol moieties on lactic acid. Oligomer formation increases as lactic acid concentration increases. The water produced by the esterification can be removed, resulting in solutions with high oligomer concentrations. Reaction of a concentrated aqueous lactic acid solution with ethanol results in oligomer esters. A model is developed for oligomer distribution in concentrated aqueous lactic acid solutions, and extended to multicomponent VLE in mixtures involving lactic acid and ethyl lactate oligomers.

Experimental data are essential, but also important is a reliable method to estimate vapor pressure of bio-derived chemicals. This work evaluates the Step Potential Equilibria and Dynamics (SPEAD) molecular dynamics method for predicting vapor pressure of secondary alcohols and esters. The SPEAD parameters for -OH and -COOH groups are obtained from the training sets, $\text{CH}_3\text{CHOH}(\text{CH}_2)_n\text{CH}_3$ and RCOOR' ; where $n = [0,6]$, $R = n$ -propyl, n -butyl, n -decanyl, n -tetradecanyl and $R' =$ methyl, isopropyl, n -butyl and isobutyl. The testing sets include 3-pentanol, 3-hexanol, 3-heptanol, and $\text{CH}_3(\text{CH}_2)_{10}\text{COOR}''$ where R'' is -CH₃, -CH(CH₃)₂, -CH₂CH(CH₃)₂, and -CH₂-(CH-Et)-Bu. The average error in prediction is ~25% of the experimental literature values for both alcohols and esters over the experimental temperature range. The evaluation of SPEAD is extended to vapor pressure prediction for molecules having multiple functional groups.