

Synergic use of Linear Free Energy Relationships and PC-SAFT

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Abstract

Second-generation lignocellulosic biomass is a promising alternative to fossil raw materials, offering sustainability, economic accessibility, and minimal competition with the food chain. It can convert cellulose, hemicellulose, and lignin into valuable chemicals, with levulinic acid standing out for its potential to produce high-value products such as alkyl levulinates and γ -valerolactone (GVL). Alkyl levulinates—methyl, ethyl, propyl, and butyl levulinates—find applications as solvents, food and fuel additives, and fragrances. GVL is recognized as a green solvent, further highlighting the diverse uses of products derived from levulinic acid. Despite its advantages, utilizing lignocellulosic biomass poses challenges, particularly in the pre-treatment phase. The biomass consists of a complex mixture of cellulose, hemicellulose, and lignin, typically processed with an acidic water-alcohol mixture. This step involves multiple simultaneous reactions, making the solvent's role crucial. A key tool for studying these reaction systems is the linear free energy relationship, which allows for the prediction of equilibrium and reactivity. This approach can significantly reduce the number of experiments, saving time and cost. However, the method is highly dependent on specific operating conditions, such as temperature and concentration. This study employed the Kamlet Abboud Taft (KAT) equation to analyze the esterification of levulinic acid with ethanol in different solvents, including GVL, water, and excess ethanol. The aim was to identify the most efficient solvent based on their properties. The second part of the research focused on the Taft equation to investigate the structure-reactivity relationships in the esterification of levulinic acid with various alcohols (methanol, ethanol, n-propanol, n-butanol, and 2-chloroethanol). The study re-estimated the polar and steric parameters for this esterification process in the 20-50°C temperature range. This re-estimation was necessary as previous literature values were only available at 25°C and under arbitrary conditions. The study hypothesized that reaction conditions, including solvent choice, might impact reaction kinetics or equilibrium, thus affecting the validity of earlier data. To standardize the analysis, esterification reactions with alkyl alcohols were carried out in water as a common solvent. This choice was motivated by the need for consistent conditions in both acidic (for esterification) and basic (for saponification) media. Water proved to be a suitable solvent for both processes. The experiments were conducted in a batch reactor under isothermal conditions, and kinetic models were developed using a Bayesian approach. This analysis yielded values for the apparent rate constant, activation energy, equilibrium constant, and reaction enthalpy at a reference temperature, with associated 95% credible intervals. These data were subsequently employed in the KAT equation to re-estimate the polar and steric effects of the substituent groups. The study also noted that the use of derived Taft substituent parameters for predicting thermodynamic and kinetic behavior does not account for certain reaction conditions, such as solvent, temperature, and concentration. To address this, the study explored the use of thermodynamic activities, specifically the PC-SAFT (Perturbed Chain Statistical Associating Fluid Theory) model, to predict solvent effects. However, the PC-SAFT model results are not consistent when varying the R-substituent group in the reaction. As a result, the study represents the first attempt to develop activity-based Taft substituent parameters by constructing activity-based models for the esterification of levulinic acid with alkyl alcohols. Concluding, this study contributes to the broader goal of biomass valorization, which is critical for the development of sustainable and renewable chemical processes.