Measurement and Predictive Modeling Using the Kamlet-Taft Parameters for Supercritical Fluid Solvents

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Serious limitations exist in equation of state modeling that use only physical properties of the solute and solvent to model supercritical and near critical solute phase equilibria. Mixing rules employed in the equation of state often include interaction parameters that are required to accurately model experimental results in an attempt to account for the interactions of the solute and solvent due to their often disparate chemical nature. Predictive models based on both physical properties of the solvent and terms to account for solute-solvent interactions will be a significant general improvement in the design of phase equilibria prediction.

Values for these solute-solvent contributions to the solution process can be obtained from solvatochromic shifts of selected probes as suggested by Kamlet and Taft. The Kamlet-Taft parameters are used to describe the hydrogen bond donation and acceptance abilities, the polarity and polarizability of the solvent. Additionally, a solvent cavity term best described by the Hildebrand solubility parameter is included. The Kamlet-Taft parameters are solvatochromic properties of the solvent determined by the energy of the longest wavelength transition of probe solutes. Rather than measure ground state properties of the bulk solvent, solvatochromic shifts measure effects at the molecular level that occur within solute-organized solvation shells and exemplify specific solute-solvent interactions present in true solution equilibria.
With the phase-out of production of many chlorinated solvents by the Montreal Protocol, replacement solvents must be evaluated in a systematic manner as potential replacements for chlorinated solvents used historically by industry; therefore, we have chosen the fully or partially fluorinated hydrocarbons as model systems to study. Unlike their chlorinated analogs, many alternative solvents are gases under ambient conditions. The thermophysical properties of the alternative solvents allow both conventional liquid-liquid extraction and the tunable solvent strength offered by near critical and supercritical fluid extraction.

The Kamlet-Taft parameters of the alternative solvents are being determined in a high-resolution UV-visible spectrophotometer. Results indicate that a continuum exists between the vapor-liquid-supercritical regions of the fluid phase diagram and that the spectroscopic transitions can easily be modeled as a function of fluid density. Multivariate statistical analysis is used to correlate the contributions of each Kamlet-Taft parameter to a given solution process. As an example of the utility of the Kamlet-Taft approach, solid-fluid equilibria will be empirically modeled in supercritical fluids.