

## Limiting Activity Coefficients In Liquids For Dilute Solutions Processes

A facile and accurate representation of the thermodynamics of fluids is essential for the rational design of separation systems. In new plants in the chemical process industry the capital costs for the separation steps are about 70% of the total cost, and the energy costs for separation average 90%! A knowledge of the phase behavior of the materials involved, and most especially of liquid phases, can permit not only the design of less expensive processes, but also can reduce contingency costs. Our goal is to define experimental methods for the rapid and accurate acquisition of the minimum number of experimental data to permit the development of readily usable mathematical models. In this proposal we deal with three types of situations -- dilute solutions and specialty separations in liquid solvents, supercritical fluid (SCF) extraction, and reaction modification to permit more facile separations.

We focus on the infinite dilution activity coefficients -- these have more information content than traditional VLE data, and they are easier to measure, correlate and predict. We develop methods to predict  $\gamma^\infty$  using new techniques based on the very successful linear free energy relationships of Kamlet, Taft, and coworkers. These use readily available measures of polarizability, polarity, acidity, and basicity to correlate configurational properties of a wide variety of solvents, and we have experience applying such methods for  $\gamma^\infty$  for both organics and water, as well as for partial molal enthalpies, which represent the temperature variation of  $\gamma^\infty$ .

We then use the best  $\gamma^\infty$  values available to estimate  $gE(x)$  expressions for binary and multicomponent systems, which can then be used for preliminary design of separation equipment. These designs can be tested for their sensitivity to the parameters used and to determine which, if any, need to be measured experimentally. This minimizes experimental data taking, and thus permits faster, less expensive, more reliable design of separation and reaction processes.