Limiting Activity Coefficients of Semihydrophobic Volatile Organic Compounds in an Extended Environmental Temperature Range

V. Dohnal[C,S]
Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic
dohnalv@vscht.cz

An efficient methodology is described for the determination of the limiting activity coefficients of semihydrophobic volatile compounds in the temperature range from the melting point to the normal boiling point of water. The class of semihydrophobic volatile solutes is delimited here by the practical feasibility of employing solution calorimetry and of determining the pure component vapor pressures with acceptable accuracy. For such solutes, a number of experimental techniques to determine the limiting activity coefficients exist, and their majority is in use in the author's laboratory. A brief overview of these techniques and their applicability is given. The essential feature of our methodology consists of combining the information on limiting activity coefficients with the information on respective derivative thermal properties, i.e. dissolution enthalpy and heat capacity, obtained by calorimetry. Employing our recently refined flow mixing microcalorimeter, we can measure the infinite dilution dissolution enthalpy very accurately as a function of temperature in the range 283 to 318 K, and thus infer the dissolution heat capacity using the temperature derivative. Alternatively, the dissolution heat capacity can be obtained as a difference between the infinite dilution partial molar heat capacity determined by heat capacity measurements of highly dilute solutions and the heat capacity of the pure liquid solute. The equilibrium and thermal data measured by us are further supplemented with critically evaluated data from the literature (if any), and the entire database is then correlated simultaneously with a suitable fitting equation using weighted regression. Data uncertainties providing statistical weights may be readjusted by trail and error to achieve the coherence of all data in the statistical sense. Routinely, a three parameter equation based on the assumption of a temperature independent heat capacity of dissolution is used, because, except for a few solutes, information on the temperature dependence of the dissolution heat capacity is missing or insufficient. Application of the developed methodology is exemplified for several solutes studied recently.