Modeling the Temperature Dependence of the Henry's Law Constant of Organic Solutes in Water

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The observed relationship between the logarithm of Henry's law constant and inverse temperature for organic solutes in a water solvent is not linear, particularly at elevated temperatures. The Henry's law constant of a particular solute goes through a maximum value at a temperature that is characteristic of the solute. This behavior causes the van't Hoff equation to fail as a general data correlation tool. Even a common chemical like toluene has a Henry's law constant at 100°C that is 60 percent lower than the value predicted by a van't Hoff extrapolation from reliable near-ambient data. Understanding how to better predict and correlate Henry's constant data versus temperature can contribute to improved designs of water treatment equipment. For example, accurate VLE predictions at temperatures approaching 100°C can avoid poor contaminant removal in packed steam stripping columns by accounting in the design process for a lowered Henry's law constant relative to a simple van't Hoff estimate. To address this data need, a chemical structure-based model has been developed to predict an organic chemical's Henry's law constant over a wide temperature range, i.e., from ambient conditions to temperatures approaching 100°C. The model combines fundamental solution thermodynamics principles with additive group and bond contributions. A literature database of over 650 critically-evaluated data points, covering six orders of magnitude in volatility, has been assembled to develop and validate the calculation method. The model, which is simple to apply, predicts the aqueous Henry's law constant as a function of temperature for alkanes, alkenes, alkylcycloalkanes, and alkylbenzenes. Accuracy of the predictions has been verified by experimental results for several substituted aromatic solutes using a modified Equilibrium Partitioning in Closed Systems (EPICS) methodology.