Thermodynamic and Phase Behavior of Supercritical Water: Organic Pollutant Mixtures

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The importance of equation of state models is fundamental to new technologies, such as supercritical water oxidation for the destruction of organic pollutants. Considering the extremely large number of existing environmentally significant chemicals, it is obvious that there is a need for the development of theoretically sound methods for the prompt estimation of their phase behavior in aquatic medium at supercritical conditions. Recent developments of the global phase diagram studies of binary mixtures make available a visualization of the entire variety of the water – organic pollutant phase equilibria. The mapping of the global equilibrium surface in the parameter space of the equation of state model offers the most comprehensive system of criteria for predicting the binary mixture phase behavior.

The most important goal of the present work is to demonstrate some fundamental links that exist between the studies of global phase diagrams and the prognosis of the thermodynamic and phase behavior of supercritical water – organic pollutant mixtures.

The main types of phase behavior for organic pollutants in aqueous environments are considered using structure-property correlations for the critical parameters of substances. Analytic expressions for the appearance of azeotropy in binary mixtures are derived for cubic equations of state with a one-fluid approximation. A local mapping concept is introduced to describe the saturation curve of water thermodynamically and consistently. The key classes of organic pollutants (polycyclic aromatic hydrocarbons - PAH, polychlorinated biphenyls - PCB, polychlorinated dibenzo-p-dioxins and furans, and selected pesticides) are considered and sources of the thermodynamic property data are examined. Vapor pressure, heat of vaporization, and critical parameter estimations as individual properties for pure components were chosen in order to seek a correlation between the octanol – water partition coefficients, KOW, and the EoS binary interaction parameters, k12. The assessment of the thermodynamic and phase behavior of different pollutant representatives is given.