Thermodynamic Properties of Hydration for Organic Solutes: Data Needs and Determination

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Thermodynamic properties of hydration (TPH) express the difference between the property of a solute in the standard state of infinite dilution at a given temperature and pressure and that of an ideal gas at the same temperature and reference pressure of 0.1 MPa. Thus, they characterize the transfer of a solute from a state where molecules are not interacting to the state where the solute molecules interact solely with the water solvent. Due to this definition, TPH can be used conveniently in physical chemistry for testing and developing theoretical models and molecular simulation for dilute aqueous solutions. At the same time, they allow for an easy calculation of distribution coefficients (such as the Henry's law constant, air-water partition coefficient, and relative volatility) of interest for chemical engineers and environmental chemists. In addition, TPH at high temperature / high pressure are useful for characterizing phase and chemical equilibria in hydrothermal systems and to guide the development of geochemical prediction schemes for aqueous fluids.

TPH cannot be directly measured but are calculated from the experimental data characterizing aqueous and pure solutes that result from phase equilibrium, calorimetric, and volumetric measurements. Unfortunately, only a limited amount of reliable data on TPH is available in the literature and therefore an international data project under auspices of IUPAC and the International Association for Properties of Water and Steam (IAPWS) has been recently started (http://www.iupac.org/projects/2004/2004-036-1-100.html). Its objective is to establish TPH for approximately 200 selected organic solutes and several inorganic gases at reference condition of 298.15 K and 0.1 MPa, and also at high temperature and pressure, provided that the data are available. In selecting the solutes, three main criteria are observed: i) coverage of the widest range of molecular structures, ii) availability of reliable experimental data, particularly with regard to the HT/HP region, iii) technological and environmental importance of individual solutes. TPH covered in the project are: the Gibbs energy of hydration and its temperature and pressure derivatives directly related to experimental data (the enthalpy of hydration, the heat capacity of hydration, and the partial molar volume at infinite dilution). A particular effort will be made to present thermodynamically consistent data at 298.15 K and 0.1 MPa that would allow calculation by integration of the Gibbs energy of hydration to at least 373 K.

The lecture will overview the philosophy, the methodology, and the current status of the project. Particular attention will be paid to the problem of data availability, their selection and consistency evaluation, and the establishment of recommended values.