A Design of a New Equation for the Description of the Temperature and Pressure Dependence of the Standard Partial Molar Volume of Organic Solutes in Water

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With an increasing amount of experimental data on partial molar volumes of nonelectrolytes in dilute aqueous solutions, there is a need for functions correlating partial molar volumes at infinite dilution in extended ranges of temperature and pressure. Several functions have been proposed in the literature and tested using data for several hydrocarbons, alcohols, ethers, and ketones. The accuracy of the data used for the tests was not sufficient for a detailed evaluation of the performance of the functions, and an average deviation over entire experimental temperature and pressure ranges was selected as a main criterion.

In this work, a new equation has been proposed for a correlation of the partial molar volume at infinite dilution in aqueous solution dependence on temperature and pressure. The standard partial molar volume of a solute, 2, in water, 1, can be evaluated from experimental data using the formula: $V_2 = [M_2 - a/\rho_1]/\rho_1$, where a is the limiting slope of the experimental dependence of the density of the solution on the molality of the solute. The proposed equation expresses the dependence of the parameter a on the temperature and density of pure water, and is divided into low density parts (the ideal gas and the second virial coeficient) and high density terms. The equation has been tested using accurate data available for several organic solutes in the temperature range from 298 to 573 K and at pressures up to 30 MPa.