

Organic Solutes in Hydrothermal Systems: Ionization Constants and Standard Partial Molar Volumes of Aqueous Hydroxy Carboxylic Acids, Amines and Amino Acids at Temperatures up to 325 °C and Functional Group Additivity Effects

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Thermally-stable, polar, polyfunctional organic solutes are being used as molecular “probes” to explore solvation effects in high temperature water. Apparent molar volumes for over a dozen aqueous hydroxy-carboxylic acids, hydroxy-amines and amino acids, and their salts at temperatures from 150 °C to 325 °C and pressures as high as 20 MPa. Chemical equilibrium constants for the ionization of several of these solutes have been measured at temperatures from 75 to 325 °C and pressure $p = 18$ MPa, using UV-visible spectroscopy with a high-pressure flow cell and thermally-stable colorimetric pH indicators. The standard partial molar volumes V_2° for the hydroxyamines and most hydroxycarboxylic acids show increasingly positive values with increasing temperature. This suggests that the Krichevskii parameter, $A_{12} = V_2^\circ(\rho^*RT)$, which describes the discontinuities in standard partial molar properties at the critical point of water, is positive, consistence with most other neutral solutes. Measurements on the isomers of hydroxy-propionic acid and hydroxy-amines suggest that functional group additivity in V_2° is obeyed to within $\sim 3 \text{ cm}^3\text{-mol}^{-1}$. The exception to this behavior is tartaric acid, which deviates quite significantly from functional group additivity, and glycolic acid (HGly). The standard partial molar volumes V_2° for HGly are relatively independent of temperature until $t > 315$ °C, at which point V_2° (HGly,aq) deviates sharply towards negative values. This is the first negative value reported for any organic molecule, and only the third ever observed for a neutral species (the others are B(OH)_3° and $\text{H}_3\text{PO}_4^\circ$). Amino acids also show negative Krichevskii behaviour, because these zwitterions have a sufficiently large dipole moment to cause significant solvent polarization at high temperature and pressure.

The temperature dependence of V_2° for these solutes from 150 °C to 325 °C can be described by a simplified form of the Sedlbauer-O'Connell-Wood equation of state. A preliminary functional-group additivity model based on these results will be presented. There is now a strong possibility of using functional group additivity models for neutral organic solutes and their salts from the present limit of 250 °C up to the critical point of water. These new data are being used to develop “equations of state” for estimating temperature- and pressure-dependant standard partial molar properties, and models for predicting the Krichevskii parameter which describes the limiting behavior of solutes at the critical point of water. Substantial challenges remain in completing the data base needed to refine such models, and in extending these experimental techniques to complex ions, high ionic strength media, and super-critical conditions.