Group Additivity in High-Temperature Aqueous Solutions: How to Account for Proximity Effects?

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Thermodynamic data for organic compounds in high-temperature aqueous media exist for a growing amount of solutes at temperatures to 300 °C. Apart from solubility measurements, large body of experimental results was acquired during the last two decades for calorimetric and densimetric properties. A few complex predictive approaches utilizing the group contribution assumption for aqueous organics at high temperatures are available (see Majer et al., 2004, for review). The group contribution schemes provide predictions up to 250 °C, but lead to substantial errors namely for solutes that include several non-alkyl functional groups in the molecule (Sedlbauer and Jakubu, 2008). The problem of proximity effects stems from the variation of electron distribution in the same functional group present in different molecules due to different nature of neighboring groups. Quantum mechanical calculations allow the estimate of charge distribution in a molecule, leading to charges and dipoles of functional groups constituting this molecule. Similar idea was presented by Lin and Sandler (2002) with an example of group contribution method for Henry's law constant at ambient conditions. The purpose of this paper is to extend their approach to a variety of thermodynamic properties and use the theoretical results for development of a corrected group contribution scheme for aqueous organics in a wide range of temperatures and pressures. Major advantage of this method is the explicit consideration of structural peculiarities of a given solute by correcting the common group contribution approach with electrostatic corrections calculated from *ab initio* principles.

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[3] Sedlbauer J., Jakubu P. *Industrial&Engineering Chem. Res.* **47**, 5048-5062 (2008).