Application of the Group Additivity Approach to Polyfunctional Aqueous Organic Solutes

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Thermodynamic properties of the (dilute) aqueous organics that are used in applications often result from predictive schemes based on a group contribution approach or another quantitative structure-property relationship. Various prediction methods are available today for aqueous organic solutes at ambient conditions; most of them apply to one property of practical interest, usually the Henry's law constant, solubility, or limiting activity coefficient. Only in recent years have there appeared models allowing us to extrapolate the properties of organic solutes at high temperatures and pressures (see [1] for review).

Soon it became clear, from the predictive attempts, that polyfunctional compounds (i.e. molecules containing several functional groups different from those constituting the hydrocarbon backbone) pose a challenge to any structure-property relationship. To overcome the problem, essentially three approaches have been suggested:

1) Applying structural corrections to simple first-order group additivity or devising higher-order group additivity schemes;
2) Correlating the structure of the solute numerically using molecular descriptors;
3) Calculating the distribution of a charge in the molecule using some quantum mechanical procedure, and applying appropriate charge distribution corrections.

Focused experimental efforts, mainly in the last decade, allow us to look in more detail at the group additivity deviations for polyfunctional organic solutes. We have collected a large part of the available literature results of thermodynamic properties in dilute aqueous solutions of organic compounds, including derivative properties (standard molar volume, enthalpy, and heat capacity) and results at elevated conditions. In this contribution, an analysis of the data will be provided regarding the magnitude of the property/temperature trends in the polyfunctional corrections to the first-order group additivity approach for standard thermodynamic properties. Based on the analysis, we have a few recommendations for further developments of the corrections.

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[1] V. Majer, J. Sedlbauer, and R.H. Wood, *Calculation of Standard Thermodynamic Properties of Aqueous Systems at Elevated Temperatures and Pressures* In D. Palmer, *et al.* (ed.) "Steam, Water and Hydrothermal Solutions: The Physical Chemistry of Aqueous Systems at Elevated Temperatures and Pressures," Elsevier, pp. 99-147, 2004.