What Additional Measurements Are Necessary to Improve the Usefulness of Group Contribution Methods for the Thermodynamic Functions of Hydration of Aliphatic Ethers, Nitriles, and Amines?

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We compiled extensive data sets leading to the values of the thermodynamic functions of hydration at 298.15 K, 0.1 MPa for aliphatic ethers, nitriles, and amines. These data are employed to determine the numerical contributions of the first and the second (Benson) order functional groups. Disappointing gaps in data make determinations of some groups' values impossible, thus limiting the usefulness of estimation methods. Specific examples will be given and discussed. This problem is particularly acute for polyfunctional compounds. There are multipole interactions between polar groups in these compounds, i.e. interactions which are absent in monofunctional compounds. The dipole-dipole interactions are of relatively long range, and they are expressed beyond the nearest neighbors, which is the range of interactions explicitly accounted for by the second order method. In order to quantify these additional effects, experimental data are necessary for polyfunctional compounds where polar groups are separated by up to 4-5 methylene groups.