Fundamental Investigation into the Solvation of Biomolecules

Sarah C. Rutan, Ernst Bezemer and John Craig
Department of Chemistry

An understanding of the structure of liquid solutions is required for understanding interactions in a broad range of biological systems. Water is a ubiquitous fluid which is involved in some level in virtually all biological reactions. In addition, other liquids are frequently used as solvents in bioanalytical methods for characterization of a vast range of complex biological samples. Specifically, liquid chromatography is a widely employed technique for the separation of the component molecules found in these samples. Two of the most common mobile phase mixtures used for liquid chromatographic separations are methanol/water and acetonitrile/water. To accurately predict the results of a chromatographic separation, an understanding of the interaction of the components of these mixtures with the biological analytes is required. Our studies focus on the elucidation of structures in methanol/water and acetonitrile/water solutions, which are as of yet still poorly understood. In our laboratory we have studied mixtures of acetonitrile and water and methanol and water by infrared spectroscopy and Raman spectroscopy and found that four unique spectra are required to describe the observed behavior. These four unique spectra should correspond to 4 unique solvent clusters with a lower binding energy than totally random molecular orientations, and with different vibrational excitations from each other.

We are using Gaussian98 at various levels of theory (up to MP2/6311** basis sets, including counterpoise correction) to calculate the internal binding energies of these clusters as well as predict their vibrational spectra. Due to constraints in time, disk space and memory we are limited to the first solvation sphere (with direct hydrogen bonding or dipole/induced dipole interactions). For water this corresponds to 4 molecules (32 unique permutations) while for acetonitrile this corresponds to 5 molecules (60 unique permutations). Some of these calculations are carried on the Beowulf Cluster located in the Bioinformatics Computational Core Laboratories.