

Calculating pK_a of Some α -Aminoacids Using Cluster-Continuum Model

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Aminoacids have several stable forms in water solutions, depending on the pH. The form in neutral solutions is zwitterionic possessing COO^- and NH_3^+ charged groups as a rule. However, all attempts to obtain aminoacids' pK_a s by theoretical methods using common thermodynamic cycles that include gas phase structures and energies of zwitterionic forms fail, because of the instability of such structures. It was found, on the other hand, that complexation with a few water molecules can stabilize zwitterionic structures [1], thus enabling use of cluster-continuum model [2] in calculating pK_a of some α -aminoacids which is a goal of our investigations.

In the present work we introduce a new approach in modelling standard reaction of solvation based on the assumption that microstructure of water solutions can be described as appropriate water clusters immersed in a dielectric continuum. These clusters of water molecules encompass solvated aminoacid as well as the H^+ and OH^- ions.

The calculations of pK_a values of the α -aminoacids require identification of the most stable conformers of water clusters formed around zwitterions and their (de)protonated structures. Reactions necessary for the calculations of basic and acidic pK_a values of some α -aminoacids selected for illustrative purposes will be discussed in detail, as well as some similarities in the cluster geometries of the most stable conformers.

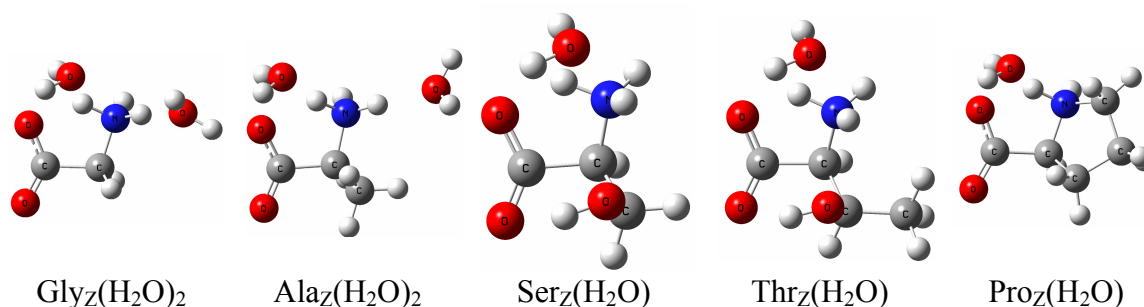


Figure 1: Most stable conformers for zwitterionic structures with minimal number of water molecules needed to stabilize zwitterionic form.

[1] J.H. Jensen, M.S. Gordon, J. Am. Chem. Soc. 117 (1995) 8159-8170.

[2] J.R. Pliego, J.H. Riveros, J. Phys. Chem. A 105 (2001) 7241-7247.