A molecular dynamics (MD) simulation of a coarse-grain polyelectrolyte chain and an all-atomistic representation of human serum albumin (HSA) was used to study the binding mechanism. MD simulation was performed using GROMACS where we include a Lennard-Jones potential to for describing the short-range interactions between protein and polyion and a screened Yukawa potential for the electrostatic interactions. The simulations were performed for a range of pH values between 6 and 11 and ionic strength between 0.01 and 0.5 M. We are able to show the existence of a critical pH, which corresponds to the onset of protein-polyion complexation. The polyion binds to the positively charged patches of HSA even in solutions where HSA carries a net negative charge. We also observe binding occurs in the absence of short-range attractive interactions, which contrasts to a previous study of a spherical model for a protein, in which case binding only occurred when including non-electrostatic forces. Further we observe that the polyion does not form loops about the protein. Within this model, we investigate the effects of polyion charge density and stiffness on the binding strength and mechanism.