Dielectric broadening as a signature of dipole-matrix interaction in protein solutions

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In this work, focused on the dielectric spectrum symmetrical broadening of water, we consider the solutions of hemoglobin (Hb) in its different states (Met-, Oxy- and DeoxyHb) both in pure water and in phosphate-buffered saline (PBS). The universal character of the Cole-Cole dielectric response enables the interpretation of the dielectric data of these solutions in a unified manner using the previously developed 3D trajectory method driven by protein concentration. It was shown that protein hydration is determined by the interaction of water dipoles with the charges and dipoles located on the rough surfaces of the protein macromolecules. In the case of the buffered solution, the transition from a dipole-ion to a dipole-dipole interaction with protein concentration is observed [1].

A new approach is proposed for evaluating the amount of hydration water molecules bounded to the macromolecule. For the solution of MetHb the amount of bound water does not change as hemoglobin concentration increased from 15 to 30 g/dL remaining at the level of ~20% of total intracellular water pool. The theoretical evaluation of the ratio of free and bound water for the hemoglobin concentration in the absence of ions corresponds with the experimental results and shows that MetHb binds about 1400 water molecules. These observations suggest that within concentration range close to physiological Hb molecules are so close to each other that their hydrations shells interact [2].

For the solution of Oxy- and DeoxyHb the changes in the number of water molecules per Hb tetramer were modest. However, the water mobility - represented by α as a function of $\ln\tau$ - differed dramatically between oxygenated state compared to the deoxygenated state of Hb at physiologically relevant concentrations (30-35 g/dL or 4.5-5.5 mM). At these concentrations, oxygenated hemoglobin was characterized by substantially lower mobility of water in the hydration shell, measured as an increase in relaxation time, compared to deoxyHb [3].

Information provided by MDS for the concentrations of Hb close to physiological makes these measurements powerful predictors of the changes in the rheological properties of red blood cells.

References

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