Biophysical thermodynamics and kinetics. Links to soft matter physics and the new challenges

Dimitri E. Khoshtariya[a,b], Maya Makharadze[b], Tinatin D. Dolidze[b], Sophio Uchaneishvili[b], Nino Shengelia[a], Mikheil Shushanyan[b], Tatyana Tretyakova[b,a], David Waldeck[c], Rudi van Eldik[d]

e-mail: dimitri.khoshtariya@tsu.ge

[a] Department of Physics, Faculty of Exact and Natural Sciences, I. Javakhishvili Tbilisi State University, I. Chavchavadze Ave. 3, Tbilisi 0179, Georgia

[b] Department of Biophysics, I. Beritashvili Center of Experimental biomedicine, Gotua 14, Tbilisi 0160, Georgia

[c] University of Pittsburgh, Pittsburgh, PA 15260, USA

[d] Friedrich-Alexander University of Erlangen-Nuremberg, Erlangen 91058, Germany

We consider connections between thermodynamic and kinetic characteristics of globular proteins that may form nanoscopic assemblies capable of electron exchange with diversely modified conducting electrodes or other molecules. First of all, we discuss our recent results on microcalorimetric (DSC) studies of the impact of moderate destabilizing organic additives, urea and dimethyl sulfoxide (DMSO) on the thermal unfolding of model globular protein, bovine serum albumin (BSA) [1]. In the previous work we already discussed the impact of these additives on a thermodynamic pattern of another model protein, α-chymotrypsin [2]. Previously, we also discussed importance of a serious consideration of the entropic contribution (along with the conventionally considered enthalpic one) to the overall thermodynamic stability of biomolecules, such as globular proteins [3]. In overall, new DSC studies on the impact of pH and concentrations of DMSO and urea on the thermal stability of BSA indicated very rich behavior. Among other results, at pH 6.0, using the additive concentrations as high as 6.0 M, we observed lowering of the protein melting temperature (T_m) from ca 70 ^oC to ca. 53 ^oC (for cases of both additives). However, for the case of DMSO the peak area (that is a measure of the transition enthalpy), exceeds the matching parameter for urea, three times (!), strongly indicating about the important role of entropic factor, viz., the fact of a strong enthalpy/entropy compensation upon the lowering of T_m [1].

Previously we reported on the experimental results and related theoretical analysis for the electron transfer/exchange (ET/EE) process for Cu^{2+} ions as redox-active probes entrapped into the Au-deposited self-assembled monolayer films (SAMs) made of L-cysteine (Cyst) [4]. We discovered the impact of glassy dynamics on ET using fast-scan voltammetry technique and its temperature and high-pressure extensions. In the course of our subsequentl effort, we performed voltammetric studies using $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{3+/2+}$ redox-active couples as outer-sphere probes for L-cysteine SAMs regarding their stability versus the impact of temperature and pressure (the latter issue was addressed at the research group of the University of Erlangen-Nuremberg) [5]. Preliminary results on the impact of temperature and pressure indicated that: (a) Cyst SAMs undergo destabilization above temperature of 25 ^oC, whereas (b) high pressure studies up to 150 MPa demonstrated not only a good resistance against the pressure increase, but also some kind of configurational transformation within the range of 20-60 MPa followed by the subsequent saturation region. The new results we explained by the reversible pressure-induced change of the SAM configuration from the vertically-aligned SAM motif to horizontally-aligned one, with latter having lees internal free volume compared to the former one. Links to the modern soft matter issues and respective new challenges will also be discussed.

References

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