

PROTEIN ADSORPTION KINETICS AS STUDIED BY DILATIONAL SURFACE RHEOLOGY

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Dilational surface properties of aqueous solutions of proteins and their mixtures with conventional surfactants have been a subject of numerous experimental studies during the last decade. The main attention is usually paid to the near-equilibrium conditions and one usually does not take into account the conformational changes of the protein and protein/surfactant complex in the course of adsorption process. In this work the dilational surface viscoelasticity of globular (bovine serum albumin (BSA), β -lactoglobulin (BLG)) and non-globular (β -casein) protein solutions was studied at large deviations from equilibrium [1-3]. This approach gives a possibility to investigate the globular unfolding in the surface layer and the formation of loops and tails protruding into the bulk phase. To this aim the complex dilational dynamic surface elasticity was determined as a function of surface age at a given frequency of surface area oscillations (in the range from 0.01 to 0.2 Hz).

The kinetic dependencies of the surface elasticity modulus of β -casein solutions proved to be non-monotonous even for solutions without conventional surfactants. At pH = 7 these dependencies have two local maxima. The comparison with the surface properties of synthetic block copolymer solutions demonstrated that the observed maxima are connected with the transitions of different parts of β -casein chains from the proximal region of the surface layer to the distal one. The displacement of relatively hydrophilic parts of the chain into the subphase proceeds in the concentration range corresponding to the first maximum. More hydrophobic parts of the chain go into the subphase in the range of the second maximum at higher surface pressures. The dilational surface elasticity of the solutions of β -casein mixtures with conventional surfactants indicates the formation of β -casein/surfactant complexes with high surface activity. The structure of the complexes changes at the increase of the surfactant concentrations leading to abrupt changes of the surface viscoelastic behaviour.

The dynamic surface elasticity of globular protein solutions increases monotonously as a function of the surface age in the course of adsorption and reaches high values ($\sim 80\text{mN/m}$). Small additions of guanidine hydrochloride or ionic surfactants results in faster changes of the surface properties as in the case of the additions of sodium chloride. However, the kinetic dependencies of the dynamic surface elasticity have a local maximum if the denaturant concentration exceeds a certain critical value unlike the case of concentrated sodium chloride solutions. This effect indicates the formation of loops and tails protruding into the bulk phase i.e. the protein unfolding. The unfolding of bovine serum albumin and β -lactoglobulin occur at different denaturant concentrations and are characterized by different kinetics.

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