Raman Optical Activity Monitoring the Interaction of Globular Proteins with Surfactants

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Nowadays many reports of ROA spectra of model proteins and polypeptides have been described, the ROA signatures being closely related with their known secondary structures.[1-2] To further progress in this direction, we report here the ROA spectra of the well-known globular protein BSA (Bovine Serum Albumin) in the presence of different surfactants which share a common hydrophobic tail. Our objective is to correlate the structural specificities of the surfactant-protein interaction with the ROA signatures by following the protein unfolding process.[3]

In its native form, BSA presents a well-structured secondary structure with an α-helix content of around 67% and turns and loops forms representing the remaining protein backbone with a large number of disulfide bridges.[4] The interaction of BSA with a variety of ligands, including fatty acids, amino acids, drugs metals, and surfactants, has been widely analyzed by many physicochemical techniques, including Raman spectroscopy.[5-6] In this communication we have studied the interaction of BSA with three selected surfactants that share the dodecyl chain as hydrophobic moiety in the forms of the anionic Sodium Dodecyl Sulfate (SDS), the cationic Dodecyl Trimethyl Ammonium Bromide (DTAB) and the neutral hexaethylene glycol monododecyl ether ($C_{12}E_6$). For each surfactant-protein ensemble, we have recorded the ROA spectra of BSA within a range of surfactant concentrations covering the pre- and post-micellar regions.

The Fig. 1 shows the most relevant ROA features of BSA in the presence of the selected surfactants. Two new groups of ROA-marker bands, unreported up to now, have been assigned to the unfolding of BSA induced by surfactants. They are related to “polar” and “apolar” protein moieties. In the first group we have the amide I and the amide III modes, which cover the 1700-1630 cm^{-1} and the 1300-1350 cm^{-1} spectral regions, respectively. Within the second group we have the methylene bending and phenyl breathing modes, which appear around 1450 cm^{-1} and 1000 cm^{-1}, respectively. The measured changes on the amide vibrations are related with the initial attack of the surfactant, which takes place through the surfactant hydrophilic heads. The vibrations assigned to the hydrophobic groups are more sensitive to the unfolding process which takes place after the hydrophilic attack.

Our work represents one of the first applications of ROA to follow the interaction of a protein with surfactants, and a new proof of the ability of this chiroptical technique to see beyond that can be seen with conventional Raman spectroscopy.

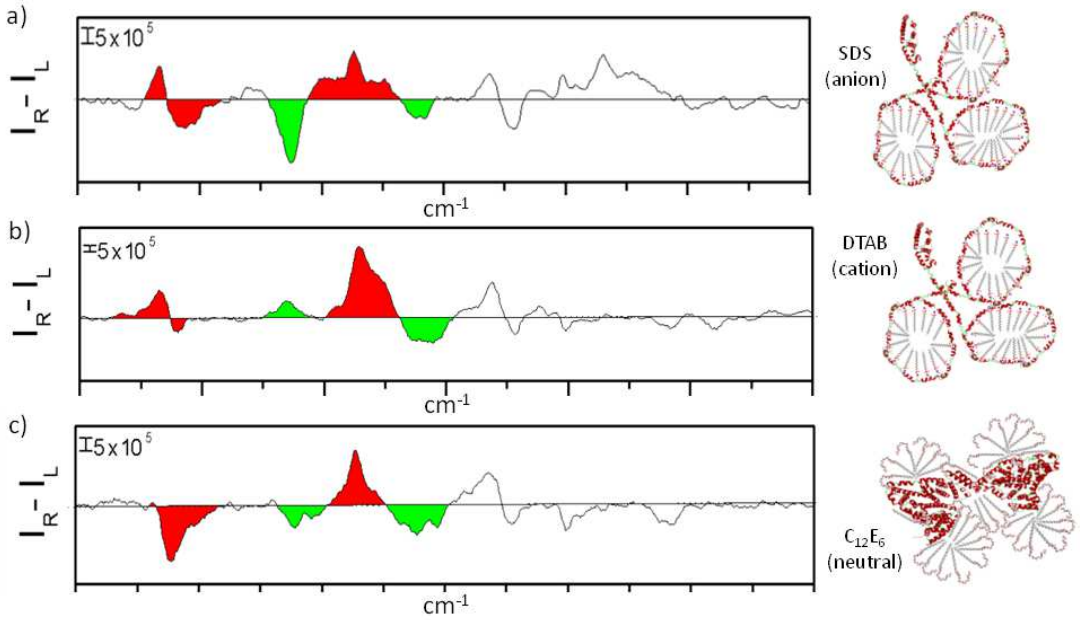

Figure 1. ROA spectra of BSA solutions in the presence of surfactants a) anionic, b) cationic and c) neutral. The most relevant ROA features have been colored in red (amide I and amide III) and green (hydrophobic moieties).

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