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Preferential solvation and optical properties of eumelanin building blocks in binary mixture of methanol and water

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ABSTRACT

Employing a sequential quantum mechanical/molecular mechanical approach for polar protic solvents, we study the absorption spectrum of eumelanin building blocks including monomers, dimers, and tetramers in pure water and methanol and three water–methanol binary mixtures having water molar fractions (Xw = 0.25, 0.50, and 0.75). The binary mixture of solvents is a common situation in experiments, but theoretical studies are limited to the use of continuum models. Here, we use explicit solvent molecules, and specific solute–solvent interaction is analyzed and seen to play an important role. Effects of the electronic polarization of solute by the environment were included using a reliable iterative scheme. The results illustrate that the monomers, dimers, and tetramers are preferably solvated by methanol, but the composition of the mixture in the vicinity of the solute molecules is different from the bulk composition with a preferential microsolvation (hydrogen bonds) in water for most species considered. It is observed that the short-range electrostatic polarization effects of the hydrogen bonds lead to a slight blue shift of the excitation energies when the concentration of water in the mixture is enhanced. For the same species, there is an enhancement of the higher-energy absorption intensity caused by long-range electrostatic interactions with the environment and that the behavior of the experimental spectrum, which is characterized by a nearly monotonic decay from the ultraviolet to the infrared, is qualitatively reproduced by the superposition of the absorption spectra of monomers, dimers, and tetramers in the liquid phase.

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