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Note

Stability of the amylose–iodine complex

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It is considered that, in the amylose–iodine complex, the helical amylose moiety polarizes the trapped iodine molecules, generating blue color in the product[1]. The stability of the complex depends[2] on such factors as the temperature, the pH, and the additives. The standard free-energy, enthalpy, and entropy of formation of the complex were evaluated by us[2] to be -10 kJ.mol^{-1}, -65 kJ.mol^{-1}, and -165 J.mol^{-1}.K^{-1}, respectively. The large-negative entropy supported ordering of the system, that is, rigidity in the conformation, as well as enhancement of the water structure. The stability of the complex is, however, least in the presence of $Na_2S_2O_3$, which reacts with iodine at the molecular level with immediate destruction of the complex. Such additives as nonaqueous solvents and urea destabilize the complex, essentially through conformational alterations. Temperature acts similarly, the effect being brought about by the increased kinetic energy of the solvent molecules, as well as of the segments of the biopolymer, reversing the decreased entropy of complex-formation.

Whatever might be the factors that could affect the complex, there is no doubt that its stability under normal conditions is quite high. The "vitality" (strength) of the amylose–iodine interaction at the molecular level was realized from the following demonstrations. We selected an amylose sample of viscosity average molecular weight 14,090, whose maximum iodine-binding capacity in 0.01M KI at 303 K, mol/mol was 12:1 as I_2:amylose.

At compositions of iodine and amylose (*a*) below saturation (5:1) and (*b*) near saturation (10:1), the samples of the complex were mixed with large proportions of benzene, shaken thoroughly, and allowed sufficient time (4 h) to attain equilibrium. It was observed that the iodine-poor sample retained all of the iodine, the nonaqueous phase being free from it. The iodine-rich sample, on the other hand, lost 20% of the total iodine present. Progressive addition of urea to the aqueous phase, up to 4M, progressively enhanced liberation of iodine into the benzene

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phase. The samples were dialyzed in dialysis tubing (Arthur H. Thomas Co., Philadelphia; diameter 22.2 mm; mol.-wt. cut-off 12,000) against benzene for one full day at 303 K; again, the iodine-rich sample released only 20% of the total iodine used for complexation. Successive dialysis with free benzene, as well as shaking with fresh portions of benzene, did not cause further release of iodine from the sample. In contrast, dialysis against surfactants (sodium dodecyl sulfate and Triton X 100) released iodine from both the iodine-poor and the iodine-rich samples. These observations led us to conclude that there are two different modes of binding of iodine to the amylose. Some 70% of the saturation capacity is very strongly bound, and the rest (~30%) is weakly associated. The first kind of affinity is so large that a nonaqueous solvent having ~360 times the affinity for iodine than has water (the partition coefficient of iodine between benzene and water at ordinary temperatures is ~360) failed to abstract it from the amylose.

The question arises as to how, under normal conditions, the binding of iodine with amylose is so strong. We presume that the answer lies in the conformation of the helical complex. The large negative entropy offers to the complex a rigid, water-protected structure through which diffusion or penetration of iodine molecules is restricted: the grooves of the helices act as traps towards the large iodine molecules. Bhide and Kale[3] reported coil-to-helix transition for the formation of the complex. Senior and Hamori[4] described a progressive diminution in the length of the amylose chain to the maximum extent of 30% after complexation with iodine. Evaluation of the effective radius of gyration through determinations of intrinsic viscosity also led to discovery[5] of a decrease in the effective radius of gyration of the iodine-deficient and iodine-rich samples to the extents of 12 and 22%, respectively. The respective Flory–Fox solvent–segment, interaction parameters[6], the α values, were 6 and 8%. This means that, upon complexation, the water activity levels decrease to these extents. The shortened helix entraps the iodine in a way which has a strong sieving-in action through the conformational architecture. To penetrate outwards, either a chemical reaction at the molecular level (such as the thiosulfate–iodine reaction) is required, or the conformation must be altered.

Surfactants and other additives (such as nonaqueous solvents and urea) act in the second way. They complex with the amylose chain and loosen the helix. Urea seems to destroy the vicinal water structure[7] and to release iodine primarily through a positive change in the entropy. There is a possibility that it also complexes with amylose.

In the temperature range of 0–70° (273–343 K), the maximum decrease in the absorbance was observed to be 30%. This can be taken as being grossly equal to the percentage change in the polarization on the iodine by the amylose chain, and, in turn, the percentage change in the segmental increase of the biopolymer. It agrees fairly well with the increment in the average radius of gyration calculated from the intrinsic viscosity already mentioned. Increase in the temperature causes lengthening of the helix, with decreased polarization of the included iodine by the polymer helix, resulting in decreased absorbance. A Van't Hoff-equation type of

analysis of the absorbance–temperature data may yield the enthalpy of this conformation-dependent process. This was evaluated to be -65 kJ.mol^{-1}. The low change in free energy (-10 kJ.mol^{-1}) and relatively large change in enthalpy indicates compensation[8] of the latter with the entropy of the system through conformational rigidity and a structured environment.

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