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Study on the Effect of an Electrolyte on the Self-aggregation and the Geometry of the Dye Aggregates of Methylene Blue in Aqueous Media

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Abstract

The self-aggregation of Methylene Blue (MB) dye in aqueous media has been investigated spectrophotometrically in presence of sodium chloride (NaCl) at 293.15, 303.15 and 313.15K. The dimerization constant (K_D) of the MB dye in aqueous solution with or without the electrolyte has been computed using a non-linear least square regression technique. It is observed that presence of the electrolyte resulted into sharp increase in K_D of MB indicating that presence of the electrolyte favours formation of dye aggregates. There is, however, a decrease in K_D with increase in temperature. From the observed spectra of the dye, the twist (θ_1) and the tilt (θ_2) angles between the dipoles of MB molecules in the aggregates have been computed based on exciton model. Change in the monomeric fractions of the dye (α) in presence of the added electrolyte as a function of the dye concentration has also been computed. The results indicated that the dye aggregates formed is essentially of the sandwich type geometry (H-aggregates) with a slight deviation from an exact parallel stacking arrangement and reduced twist angle. The thermodynamic parameters of the aggregation process in presence of the electrolyte have been evaluated from the temperature dependence of K_D. It is observed that the aggregation process is an enthalpy rather than entropy controlled one.

Keywords: Aggregate Geometry, Dimerization Constant, Effect of Electrolyte, Exciton Model, Methylene Blue