Fluorescence Studies on Interaction of N-Methyl-4-(4'-hydroxyphenyl)pyridinium salt with Cyclodextrin

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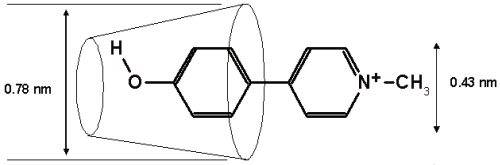
Cyclodextrins (CDx) are cyclic oligosaccharides composed of glycopyranose unit linked together via oxygen bridges at the 1 and 4 positions (α-(1, 4)-glycosidic bond). This class of organized media possesses a hydrophilic upper and lower rims lined with hydroxyl groups and a hydrophobic cavity linked ether oxygen. This structure gives CDx the ability to extract a variety of organic guest molecules of appropriate size.



Scheme 1: Structure of 4OHMPP$^+$ and inclusion complex formation between 4OHMPP$^+$ and CD

1-Methyl-4-(4'-hydroxyphenyl)pyridinium Iodide (4OHMPP$^+$) is a good substrate for membrane bound amine transporters such as vesicular monoamine transporter (VMAT) and dopamine transporter (DAT). CDx can be used as an excellent model to study the mechanism of binding and transport of 4OHMPP$^+$ through the VMAT.

The inclusion of 4OHMPP$^+$ in Cyclodextrin (CDx) was studied by fluorescence and UV-visible spectroscopy at two different pH's (4.5 and 7.4) and three different temperatures (298, 303 and 308 K). In the polar protic medium, 4OHMPP$^+$ undergoes rapid deprotaonation followed by formation of low fluorescence quinoid structure. Upon addition of CDs to 4OHMPP$^+$ in polar aqueous media, fluorescence enhancement was observed. This concludes that the guest molecule would interact with CDs hydrophobic cavity which prevents the deportanation followed by quinoid structure formation. The binding constants were determined by fluorometric data shows 1:1 stoichiometry and which fixed in to the modified Benesi-Heldbrand equation,

$$\frac{1}{(F - F_0)} = \frac{1}{(F_\infty - F)} + \frac{1}{(F_\infty - F_0).K.[fluoro\quad phore]}$$

where F and F_0 are the fluorescence intensities in the presence and in absence of CD, respectively. F_∞ is the fluorescence intensity observed when all the 4OHMPP$^+$ molecules were complexes with CD. *[fluorophore]* is the concentration of 4OHMPP$^+$ and K is the binding constant. The binding constant increases with increasing temperature. The ΔS^0 accompany the complex formation is positive and it is entropically favored. This value is attributed to the loss of structured water around the guest molecule.

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