Micelle catalyzed 4-nitrophenol reduction

In aqueous solution, molecules with both polar head group and non polar tail (amphiphilic molecules) aggregate i.e., *micelles*. They absorb/uptake both polar and non polar molecules from solution as a universal host. Thus the horizon of catalysis, detergency, pollution abatement etc. is improved with micellar solution. As micelle structures are constantly breaking and reforming, complex molecules, fatty acids vitamins, cholesterol etc. can be engulfed and transported by micelle to cell membrane and in turn diffuse through the intestinal cell wall. Keeping the absorption and transportation characteristics of suitable micelle (Fig. 1) in mind, confinement of reactants for catalysis has been thought of for 4-nitrophenol (4NP) reduction by sodium borohydride ($NaBH_4$) in aqueous medium.

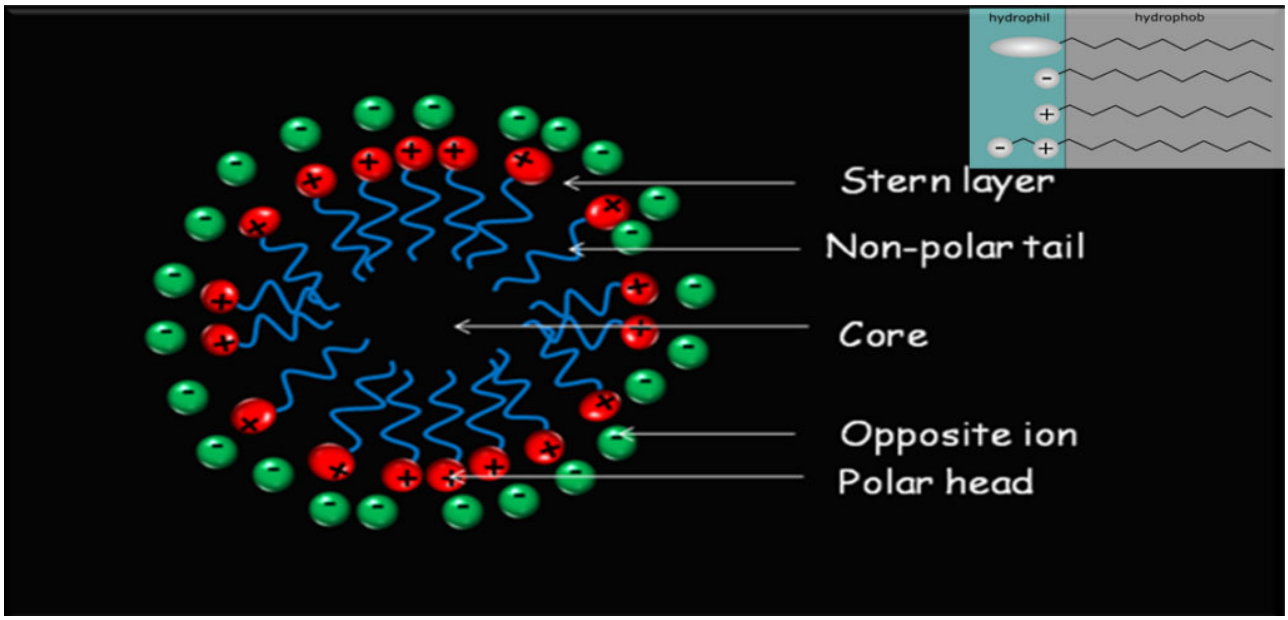

Fig. 1. Schematic representation of micelle.

In aqueous $NaBH_4$ solution the reduction of 4NP does not progress significantly even though both the species are water soluble. Only the color of 4NP intensifies with $NaBH_4$ as the pH of the solution becomes strongly alkaline. The alkaline solution gives rise to negatively charged nitrophenolate ion (4NP-) which is responsible for the intense yellow coloration. The reaction needs to be catalyzed and considering the ionic nature of the reactants it was thought that ionic micelles might have the propensity to catalyze the reaction.

Suitable anionic micelle from sodium dodecysulfate (SDS) surfactant has been employed successfully to reduce 4NP without any other catalyst support. Thus environmentally hazardous 4NP becomes industrially important 4-aminophenol (4AP). It is worth mentioning that 4AP is used

to produce paracetamol, an efficient antipyretic drug. The reduction of 4NP in aqueous micellar solution progresses satisfactorily with $NaBH_4$. Yellow color of the solution of $4NP^-$ changes to colorless 4AP in solution progressively. This indicates the on set of reduction reaction. Naked eye estimation can be made quantitative using a visible spectrophotometer at 400 nm wavelength (Fig. 2). This is an elegant example of micelle catalyzed 4NP reduction reaction. Thousands of reports have been published for 4NP to 4AP reduction employing metal and metal oxide nanoparticles. Thus the reaction, proposed from our laboratory, has been identified as a 'bench mark model reaction' all over the globe to test the efficacy of a nanocatalyst.

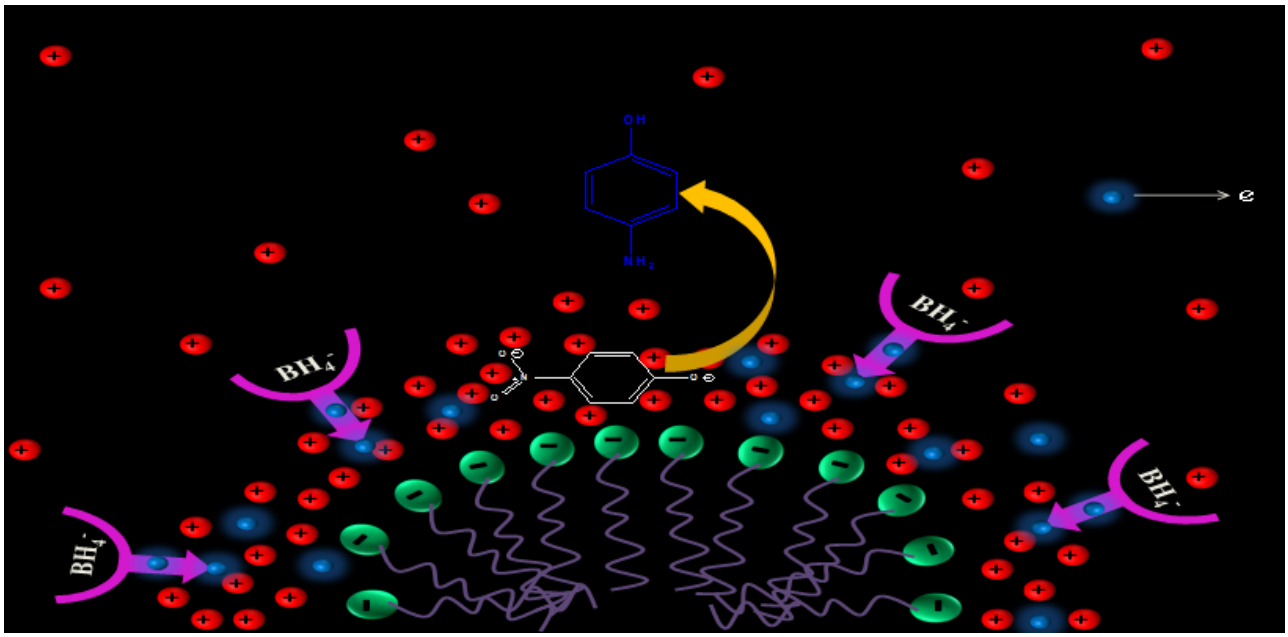

Fig. 2. Representation of 4-NP reduction in micelle catalyzed way.

Electrostatic i.e., columbic interaction dominates in the SDS catalyzed reaction. Suitable orientation of the reactants as well as co-localization effect at the water-micellar interface or at the Stern layer favors the micelle catalyzed reaction. It is proved that micellar concentration is not the exclusive driving force. Nitrophenolate ion ($4NP^-$) being a charged reactant, the most reasonable location of $4\text{-}NP^-$ ions is in the water-rich Stern layer. It is pertinent to mention that Stern layer in micelles is the layer between the core/water interface of a micelle where greater charge density of counter ions exists. This denser charge accumulation at the Stern layer is analogous to 2D graphene sheet like conducting platform to carry forward ion conduction for a reaction to happen even in solution. The most enhanced reaction rate in SDS over other micelles suggests that increased ionic concentrations at Stern layer are playing the important role in the SDS micellar system for catalysis.

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Publication

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